Modeling of Adsorption – Reaction Phenomenon on Activated Carbon

by

Ekhator Emmanuel Osagie

A Thesis Presented to the

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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THESIS ABSTRACT

NAME OF STUDENT	:	**EKHATOR EMMANUEL OSAGIE**
TITLE OF THESIS	:	**MODELING OF ADSORPTION REACTION PHENOMENA ON ACTIVATED CARBON**
MAJOR FIELD	:	**CHEMICAL ENGINEERING**
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The adsorption of phenol and its reaction with oxygen on granular activated carbon is modeled using a dual mechanism pore and surface diffusion model and the homogeneous surface diffusion model in both batch and column systems combined with a reaction term involving phenol and oxygen adsorbate concentration.

The dependence of surface diffusivity coefficient on adsorbed phase concentration is accounted for by the use of Darken's relation. From experimental studies, the rate and extent of reaction is established as dependent on oxygen availability in the system. Hence, a rate of reaction expression is incorporated in the model based on the assumption that the rate is proportional to the oxygen imbalance and the adsorbed phase concentration.

The adsorption and reaction models are tested by fitting the experimental data generated by Abuzaid(1993). The models parameters are optimized. The resulting model is in good agreement with the experimental data. Generally, the model fits obtained from the batch studies are better than those obtained from the column studies.

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ملخص الرسالة

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التخصص : هندسة كيميائية .

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امتزاج الفينول وتفاعله مع الاكسجين على حبيبات الكربون المنشط تمت صياغته باستعمال ميكانيكية مزدوجة لصورة الانشار المسامي والسطحي وصورة الانتشار السطحي المتماثل في كل من نظامي (البرجي & batch) مع حد للتفاعل بين الفينول والاكسجين الممتز على السطح .

اعتماد معامل قابلية الانتشار السطحي على تركيز الطور الامتزاجي تم احتسابه باستعمال علاقة داركن . أثبتت الدراسات التجريبية أن معدل وحجم التفاعل يعتمد على وجود الاكسجين في المفاعل.

بناءاً على ذلك فإن صيغة معدل التفاعل ادخلت في الصيغة بناءاً على الإفتراض بأن المعدل يتناسب مع اختلال توازن الاكسجين وتركيز الطور الامتزاجي .

صيغ الامتزاج والتفاعل تم اختبارها بإخضاعها إلى نتائج التجارب التي توصل إليها أبوزيد (١٩٩٣) حدود الصيغة وضعت في أفضل صورة الصيغة الناتجة على إتفاق طيب مع نتائج التجارب. بصورة عامة ، مطابقات الصيغة التي تم الحصول عليها من دراسات (batch) كانت أفضل من تلك التي تم الحصول عليها من دراسات المفاعل البرجي .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

يوليو ١٩٩٦م

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

A large number of synthetic organic chemicals are currently produced in the process industries, and several of these are introduced into the environment by accident or through poor design. Many of these compounds are of toxicological importance, causing carcinogenic, teratogenic, and mutagenic effects when ingested as part of drinking water over a long period of time.

Adsorption is the selective collection and concentration onto solid surfaces of particular types of molecules contained in a liquid or a gas. Adsorption offers an effective means of selectively separating mixtures of gases or liquids even at very low concentration. The molecules are removed from the liquid or gas stream by attachment to a variety of specific materials known as adsorbents. The material which is adsorbed onto the adsorbent is called the adsorbate.

Adsorption on granular activated carbon (GAC), is one of the most dependable and effective technologies currently available for the treatment of drinking water and wastewater's contaminated with low concentrations of hazardous compounds. Activated carbon is commonly utilised in environmental engineering due to its good adsorption characteristics for the removal of organic compounds. The removal of pollutants by adsorption onto activated carbon involves transport of an adsorbate molecule to the exterior surface of an adsorbent particle, pore diffusion and surface

diffusion, and adsorption of the adsorbate onto the interior surfaces of the adsorbent. Normally, one or more of these steps controls the process.

Activated carbon is used in various water treatment reactors. These include the fixed bed reactor, fluidized bed anaerobic reactor, and activated sludge systems. The design of contact systems and the prediction of their performance have been dependent on laboratory equilibrium data. The need for a better understanding of the nature of granular activated carbon (GAC) and it's capacity for the retention of various compounds necessitated the extensive research efforts that have been channelled in this direction.

The adsorption capacity of an adsorbent is the amount of solute it can adsorb per unit mass. It is a key component needed for the prediction of adsorber performance and it is given by an adsorption isotherm which represents the equilibrium between the quantity of adsorbate retained per unit mass of adsorbent, and the concentration of adsorbate in solution at constant temperature.

The adsorption uptake is the amount of solute adsorbed from the bulk phase as a fraction of that present initially. It is dependent on some variables that includes the size of the particle, the initial solute concentration in the bulk phase, the amount of adsorbent used, maybe the presence of dissolved oxygen and the equilibration time allowed. All but one of these variables are well known and have received adequate attention. The elusive variable, whose influence on adsorption capacity of GAC is obfuscated by its seeming indirect involvement in the phenomenon is the level of dissolved oxygen. In the involvement of dissolved oxygen lies the solution to the conundrum that has baffled many researchers. Only recently has there been a conscientious and systematic study designed to elucidate the effects of the presence of dissolved oxygen on adsorption equilibrium. The puzzling discrepancies in

the various adsorption isotherms reported is now linked to the different amounts of dissolved oxygen in the experimental set-ups. It is an established fact that oxygen adsorbed on GAC forms surface acidic oxides. These oxides are responsible for the oxidative coupling reactions occurring presumably on the surface of the carbon. This reaction is promoted by oxygen. The paramount effect of this is manifested in a change in the adsorption capacity of GAC.

Various models have been used to predict the adsorption process. In most of these models the effective diffusivity coefficient is assumed constant. However, diffusivity coefficients have been found to be concentration dependent.

1.2 Status of Adsorption in Pollution Removal

The findings of various independent researches corroborates the fact that adsorption by granular activated carbon is one of the most effective water treatment units process to remove many different types of trace organics found in drinking water (Symons, 1978).

McGuire et al. (1991) conducted a detailed evaluative study on the use of GAC for trihalomethane (THM) in water control. One of the objectives of the study was the estimation of the costs associated with optimised GAC treatment for the Metropolitan Water District of southern California (MWD) and for six other water utilities across the United States of America. GAC adsorption was found to be an expensive means of THM control. The capital costs of implementing GAC adsorption as a unit process for THM precursor removal range from $730 to $3,900 million (based on a capacity of 2,970 mgd), depending on whether the upcoming regulations are set at 50 or 5μ g/L.

1.3 Detailed Background On Granular Activated Carbon

Activated carbon can be made from a number of raw materials having a high carbonaceous content. The principal raw materials for commercially available carbons are sawdust, lignite, wood charcoal, peat, bituminous coal, and petroleum coke.

There are two principal methods for making activated carbons. In each of these methods, the starting materials is heated in the absence of air. The two principal methods are :

1. High - temperature oxidation with steam of a previously charred carbonaceous substance(coal, char, charcoal)

2. Lower temperature chemical dehydration and/or chemical reaction of a carbonaceous raw material (Perrich, 1981)

Much of the substances devolatilize leaving behind a porous structure of carbon that usually contains some hydrogen. Activation of the carbon is done by controlled oxidation with steam or carbon dioxide to further open up the pores and increase the total surface area. Precise control of both reaction temperature and time is very important in steam activation processes to impart desired properties. Temperatures usually range upwards from $800^{\circ} C$.

The activated carbon may contain up to about 10 wt % oxygen, which may cover a large fraction of the surface as chemisorbed oxygen in the form of ketones, hydroxyls, or carboxylic acids. The surface area can range up to about 1200 m^2/gm (Satterfield, 1991).Granular Activated carbons generally have particle sizes larger than 20 mesh. They are widely used in liquid phase operations.

A cross section of a portion of an activated carbon particles might look like a maze of inter connecting channels, quite large at the surface and terminating in small channels in the interior. The distribution of the pores is

basically trimodal. The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolysis and activation procedures. Typical ranges are given in Table 1.1. However, activated carbons with desired porosity, surface area, and adsorptive capacity can be tailored by special procedure.

When prepared and stored under inert environment, the surface of carbon is essentially non-polar. However, surface oxidation does occur when the surrounding atmosphere is non-inert. As a result, carbon adsorbents tends to be hydrophobic and organophilic.

Table 1.1 : Typical values of GAC physical properties.

	Micropore	Mesopore or Transitional pores	Macropore
Diameter (^{o}A)	< 20	20 - 500	0.2 - 0.5
Pore volume (cm^3/g)	0.15 - 0.5	0.02 - 0.1	0.2 - 0.5
Surface area (m^2/g)	100 - 1000	10 - 100	0.5 - 2

The particle density in the range of 0.6 - 0.9 g/cm^3 and the porosity is in the range of 0.4 - 0.6.

1.4 Scope Of This Thesis

In this study three specific areas are treated. First is the modelling of the adsorption occurring in GAC. The pore and surface diffusion model (PSDM)

and the homogeneous diffusion model (HSDM) will be used. Two cases will be considered. Case one treats the surface diffusivity as constant. In case two, the concentration dependence of surface diffusivity using Darken's relation is incorporated in the model.

The second area is concerned with adsorption with reaction on GAC in batch systems. Here, it is desired to fit our model results to experimental data where reaction has occurred. To this end, a reaction model is postulated. The attendant objective is to ascertain the optimum values of the reaction order with respect to phenol and oxygen and the reaction rate constant by minimising the root mean square deviation between experimental and model results.

The third is simply an extrapolation of the batch results to the fixed bed reactor. The kinetic parameters determined in the batch system are directly utilised here.

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CHAPTER TWO

DIFFUSION MODELS IN BATCH SYSTEMS.

2.1 Introduction :

The diffusion of adsorbate onto activated carbon involves a number of steps, each offering its own resistance. First we have diffusion through the film layer surrounding the activated carbon onto its exterior surface. This is film diffusion. Secondly, there is intraparticle diffusion which involves the transport of molecules through the solution in the adsorbent macropores (macropore diffusion), and micropores (micropore diffusion). Micropore and macropore diffusion are normally classed together as pore diffusion. Thirdly, there is diffusion of adsorbed molecules along the surface of the adsorbent. This is called surface diffusion.

External mass transfer or film diffusion is usually the rate-limiting step in systems that have poor mixing, dilute adsorbate concentrations, small adsorbent particle sizes and high adsorbate affinity for adsorbent. In contrast, the intraparticle step limits the overall transport for those systems that have good mixing, large adsorbent particle sizes, high adsorbate concentrations and low adsorbate affinity for the adsorbent. The adsorption step in physical adsorption processes is generally accepted to be very rapid (Weber and Morris, 1964). Consequently, the rate of adsorption is controlled by one of the preceding diffusional steps.

When adsorption takes place in a large vessel, the concentration of the fluid in the vessel is regarded as being constant throughout the process of

adsorption. Such a vessel is called an infinite bath and the adsorption process is conceptualized as occurring at constant boundary condition.

When adsorption takes place in a bath of finite volume, concentration of the fluid in the vessel decreases with progress of the process. Such a vessel is called a finite bath and the adsorption process is conceptualized as occurring with an unsteady state boundary condition. The diffusion in an infinite bath or a finite bath may be pore diffusion controlled, surface diffusion controlled, external mass transfer controlled, or all of these steps could play a significant role.

2.2 Literature survey :

Adsorption capacity is expressed by an adsorption isotherm which represents the equilibrium between the quantity of adsorbate retained per unit mass of adsorbent, and the concentration of adsorbate in solution at constant temperature. Isotherm data are most commonly obtained using the so called bottle-point technique. Unfortunately, a unified experimental procedure has not yet been established. The experimental approach of most researchers differ. These procedural differences reflect in the carbon preparation, particle size, and volume of container used in the experiment, volume of adsorbate solution added, buffer application and, equilibration time allowed. Consequently, a myriad of different isotherms are reported in the literature for the same combination of chemical compound and granular activated carbon (GAC). Isotherm data can also be obtained using batch reactor and column methods.

Theoretically, equilibrium data are independent of the way they are obtained and GAC capacities must be in agreement irrespective of the experimental procedure adopted. However, many researchers report that such

was not always the case (Crittenden and Weber, 1985; Van Vliet et al., 1980; Yonge et al., 1985; Liu and Weber, 1981; Reschke et al., 1986). The following explanations for the discrepancies have been suggested :

(1) continuously decreasing liquid phase adsorbate concentration during the equilibration period (Yonge et al., 1985)

(2) irreversible adsorption (Yonge et al., 1985)

(3) decline in intraparticle diffusion rate during the later part of breakthrough, as saturation is approached (Van Vliet et al., 1980)

(4) difference in diffusion processes into macropores and micropores (Peel and Benedek, 1981; Seidel and Gelbin, 1986; Seidel et al., 1985).

Adsorption isotherms assume various forms. Some are accurate only within a limited concentration range. The Freundlich isotherm falls into this category (Hand et al., 1983; Seidel et al., 1983; Chatzopoulos et al., 1994). Thus the form of the isotherm used can affect the accuracy of predictions when modeling the adsorption process. Most researchers in the past fitted phenol adsorption data by the Freundlich isotherm. The commonly used adsorption isotherms are Langmuir, Freundlich, Redlich-Peterson, (Seidel et al., 1985, Hand et al., 1983), Radke- Prausnitz, and Fritz- Schlunder (Chatzopoulos et al., 1994).

Adsorption onto activated carbon is usually an unsteady state process. The rate of adsorption is influenced by a number of parameters. The most important include the pH of the solution, temperature, initial concentration of the adsorbates, particle size, flow rate (in column) of adsorbate solution and competitive adsorption in multi-component systems.

The adsorption uptake of carbon increases with increased mass of the adsorbent (McKay and Bino, 1988) and the size of the particle used.

(Wilmanski and Lipinski, 1989; Mathews and Zayas, 1989; Cooney and Xi, 1992).

Physical adsorption is an exothermic phenomenon. Consequently, the extent of adsorption generally increases with decreasing temperature. Alben et al. (1978) observed gradual diminution of GAC adsorption capacity of trihalomethanes on granular activated carbon with increasing temperature in the range of 4 to 45 degree celsius. This trend is supported by the work of Abuzaid (1993) for the adsorption of phenol and o-cresol on GAC.

In general, adsorption of typical organic pollutants from water increases with decreasing pH. Alhert and Gorgol (1983), investigated the adsorption of the supernatant of two landfill leachates on GAC for total organic carbon with the adsorptive capacity at pH 7 greater than that at pH 2.

The adsorption process has been represented in the past by a variety of models. In the homogeneous surface diffusion model (HSDM), first used by Rosen (1952) to describe adsorption kinetics from aqueous solutions, an isotropic adsorbent particle with a narrow pore-size distribution is assumed. Rosen (1952) used a linear isotherm. The HSDM has been successfully applied for non-linear isotherms (Fritz et al. 1983; Hand et al., 1983). Also, adsorbate molecules are assumed to creep along the abundant inner surfaces of the adsorbent in the adsorbed state. In the pore diffusion model (PDM), first used by Edeskuty and Amundson (1952), transport of molecules is assumed to take place in the liquid phase of the adsorbent pores. The pore and surface diffusion model (PSDM) was proposed by Weber and Chakrovorti (1974), and Fritz and Schluender (1974) in which simultaneous occurrence of surface and pore transports in significant amounts are assumed. GAC however, contains a wide range of pore sizes (Famularo et al., 1980; Peel and Benedek, 1981). Adsorption rates in most modeling studies have

been described using the "homogeneous" particle models. This is primarily because of the small number of solute transport parameters involved and the low computational effort required for the solution of these models. Previous studies showed that the dominant mechanism of intraparticle solute transport for activated carbon adsorption of organics from aqueous solutions is by surface diffusion (Neretnieks, 1976; Fritz et al.; 1981; Hand et al.; 1983).

Until recently, activated carbon adsorption of organics from aqueous solutions was most commonly described by the homogeneous surface diffusion model (HSDM). The HSDM is also called the solid diffusion model (Hand et al., 1983; Al-Duri and McKay, 1991, Vidic et al., 1994; Chatzopoulos et al., 1994). In most cases, the surface diffusion coefficient D_s was assumed to remain constant throughout the adsorption process. However, there has been considerable evidence that D_s increases with surface loading both in single component and multicomponent solutions (Sudo et al., 1978; Al-Duri and McKay; 1991, Vidic et al., 1994). This phenomenon has been well established for the diffusion of gases on solid surfaces and can be explained by the energetic heterogeneity of the surface, the increase in the mean free path of surface diffusion with surface loading and the lateral interactions among the adsorbed molecules at high surface coverages (Sudo et al., 1978; Kapoor et al., 1989, Chatzopoulos et al., 1994; Vidic and Suidan, 1994). In addition, a $D_s(q)$ dependence also arises when the solute diffusion flux is represented in terms of the chemical potential gradient rather than the concentration gradient on the surface (Sudo et al., 1978; Ruthven, 1984).

Kapoor et al. (1989) presented a review of existing models for the concentration dependence of the surface diffusion coefficient in gas solid systems. Among these models, the one proposed by Gilliland et al. (1974) has been widely used to describe the dynamics of adsorption from dilute aqueous

solutions (Neretnieks, 1976; Muraki et al.; 1982; Seidel and Carl, 1989). This model assumes an implicit exponential dependence of D_s on the surface concentration. A correlation similar to this form was used by some researchers to account for the concentration dependent D_s. (Chatzopoulos et al., 1994).

Some researchers fitted adsorption rates in finite bath batch systems with the assumption that D_s remains constant throughout the course of the adsorption and observed that the resulting D_s values increased with initial solute concentration in the solution. (Neretnieks, 1976; Sudo et al. 1978; Fritz et al. 1981; Itaya et al., 1987; Al-Duri and McKay, 1991; Chatzopoulos et al., 1994, Vidic et al., 1994).

McKay and Bino (1985), fitted the adsorption data by a model based on external mass transfer and pore diffusion. They observed a deviation from theory which they attributed to a probable change in D_s with varying extents of adsorption in line with Peel and Benedek's (1981) branched pore theory. The extent of adsorption is noted to be a function of pore size distribution within the particle and the relative size of the solute molecules.

Wilmanski and Lipinski (1989) after a study of the activated carbon adsorption kinetics of total organic carbon from water in a batch reactor reported that the effective pore diffusion coefficient continuously decreases as the total organic carbon removal on activated carbon proceeds. They claimed that this phenomenon can be substantially limited after reducing the carbon particle diameter to a value of about 0.1 mm. The effective pore diffusivity is reported to have an inverse relationship with the diameter to the particles used in the adsorption process. This is in agreement with the work of Randtke and Snoeyink (1983) and Crittenden et al. (1984).

Vidic et al. (1994) reported a variation of D_s in a closed batch kinetic experiment with initial adsorbate concentration in the liquid phase and this is in accordance with the findings of Komiyama and Smith (1974) and Gilliland et al. (1974). They showed that there is a linear relationship between the equal surface loading and the best fit D_s value when different initial adsorbate concentrations are used. Sladek et al.(1974) observed that for both physically and chemically adsorbed species, the activation energy for the formation of a vacant site adjacent to the adsorbed molecule decreases with an increase in surface coverage. This is a direct consequence of a decrease in the bonding energy of adsorption, which represents a fraction of the heat of adsorption, for higher concentration of adsorbate molecules on the carbon surface. As a result, the movement of adsorbate molecules intensifies and, consequently the surface diffusion coefficient increases.

Hu et al. (1993b) investigated the effect of the concentration dependence of surface diffusivity in binary adsorption, desorption and displacement kinetics under various conditions. They used the macropore, surface and micropore diffusion (MSMD) and the constant surface diffusivity macropore, surface and micropore diffusion (CMSMD). Of these two, the results given by the MSMD model were superior since it accounted for the concentration dependence of surface diffusivity. However, the CMSMD fitted single component system very well by using different bulk concentrations (Hu et al., 1993a). The effect of concentration dependent surface diffusion was noted to be most significant at low temperatures and with small particles. The high dependent level at low temperatures is a result of the great contribution of diffusion to the transport process.

Various attempts of theoretical work to quantitatively predict the concentration dependence of surface diffusivity have been devoid of promise

(Higashi et al., 1963; Yang et al., 1973; Chen and Yang, 1991; Do et al., 1992). Noting this, Hu et al. (1994) devised a new experimental procedure to be used with the differential adsorption bed to determine the intrinsic concentration dependence of the surface diffusivity of hydrocarbons in activated carbon. They employed the pore and surface diffusion model. Ethane and propane were used in the experimental work. The pore diffusivities used in the model were calculated from standard correlations. Along with the experimental work, a theoretically based investigation was conducted solely for the purpose of comparison. The theoretical prediction was based on the chemical potential gradient as the driving force. This reduces to the Darken's relation. Juxtaposed with the experimental results, the Darken's relation gave a very poor prediction of the concentration dependence of the surface diffusivity. This has also be reported by Gutsche and Yoshida (1994). The experimentally determined surface diffusivity roughly follows Darken relation if the amount adsorbed is less than 1 mmol/g. However, when the amount adsorbed is more than 1 mmol/g, the increase of surface diffusivity with loading is much faster than that calculated by the Darken's relation. The failure of Darken's relation is most pronounced along the non-linear part of the isotherm. The intrinsic surface diffusivity determined increases with both temperature and surface loading.

2.3 Theoretical Model.

2.3.1 Model Development For A Batch System

Consider a finite bath loaded with GAC particles of constant size-that is sieved to a homogeneous size of 0.156 cm. The particles may be freely suspended in the liquid phase or fixed in a wire mesh container to reduce the

film mass transfer limitation. The liquid phase generally consists of water plus the dissolved organic with or without oxygen. The bath contains an impeller and baffles. The rate of rotation of the impeller influences the mass transfer.

The following assumptions are made :

(i) the bath is finite,

(ii) the system is at constant temperature,

(iii) the adsorbent particles are isotropic with uniform pores and no preferential pore direction,

(iv) the solution is dilute so that the molecular diffusivity and the mass transfer coefficient are constant

Consider a general model incorporating all of the various adsorption resistances and steps. The first step of the overall transport process is the transfer of the solute from the bulk phase at concentration C to the surface of the particle at concentration C_s. The transport occurs by convective mass transfer and the describing equation is :

$$N = k(C - C_s) \qquad 2.1$$

where k is the convective mass transfer coefficient and N ,the mass flux, is based on the total external area (solid plus pore mouth) of the particle.

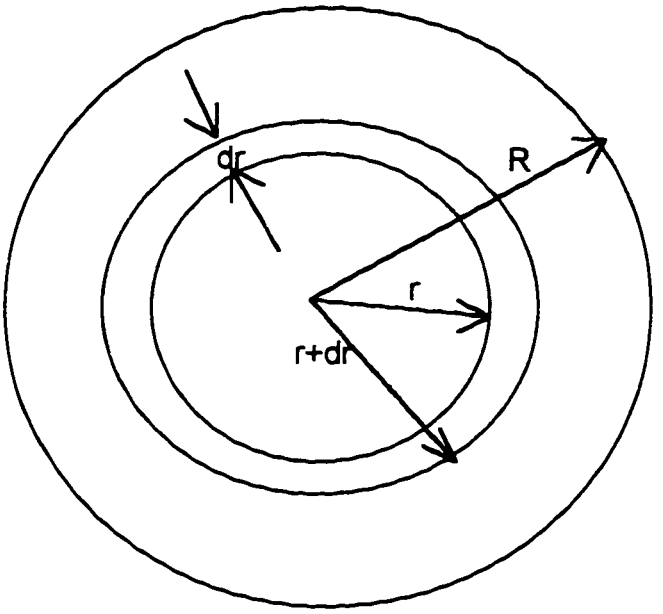
Step two is the molecular diffusion of the solute in the liquid in the pores of the particle (pore volume diffusion). This step which is in series with the first step is described by the following equation :

$$N_p = -\left(\frac{\varepsilon D_{AB}}{\tau}\right)\frac{\partial C_p}{\partial r} = -D_{e,p}\frac{\partial C_p}{\partial r} \qquad 2.2$$

where D_{AB} and $D_{e,p}$ are respectively the effective molecular and pore diffusivities.

The adsorption of the solute on the surface of the pore constitutes step three. Here, it is assumed that the concentration C_p in the pore liquid is in local equilibrium with the amount adsorbed, q at the given position, i.e., the rate of step three is reversible and fast (Furusawa and Smith, 1974). Various isotherm forms are normally used in relating q and C_p

Performing a mass balance on the shell of the particle gives



Accumulation = Input - Output + Generation - Consumption

$$4\pi r^2 \Delta r\left[\varepsilon \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial t}\right] = \left[4\pi r^2 N\right]_r - \left[4\pi r^2 N\right]_{r+\Delta r} \qquad 2.3$$

$$\varepsilon\frac{\partial C_p}{\partial t}+\rho_p\frac{\partial q}{\partial t}=-\frac{1}{4\pi r^2}\left(\frac{\left[4\pi r^2 N\right]_{r+\Delta r}-\left[4\pi r^2 N\right]_r}{\Delta r}\right)$$
$$=-\frac{1}{4\pi r^2}\frac{\partial\left[4\pi r^2 N\right]}{\partial r} \qquad 2.4$$

Assume the combined pore and surface flux to be :

$$N=-(\varepsilon D_p\frac{\partial C_p}{\partial r}+\rho_p D_s\frac{\partial q}{\partial r}) \qquad 2.5$$

$$\varepsilon\frac{\partial C_p}{\partial t}+\rho_p\frac{\partial q}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\left[\varepsilon D_p\frac{\partial C_p}{\partial r}+\rho_p D_s\frac{\partial q}{\partial r}\right]\right\} \qquad 2.6$$

Now

$$\frac{\partial C_p}{\partial r}=\frac{\partial C_p}{\partial q}\frac{\partial q}{\partial r} \qquad 2.7$$

$$\varepsilon\frac{\partial C_p}{\partial t}+\rho_p\frac{\partial q}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\left[\varepsilon D_p\frac{\partial C_p}{\partial q}+\rho_p D_s\right]\frac{\partial q}{\partial r}\right\} \qquad 2.8$$

$\frac{\partial C_p}{\partial q}$ is obtained from the isotherm equation used.

Initial conditions :

$$C = C_o; \qquad r=0$$
$$C_p = C_p(\tau,0) = 0; \quad 0 \le r \le r_s \qquad 2.9$$
$$q(r,0) = 0; \qquad 0 \le r \le r_s$$

Boundary conditions :

BC.1

$$\left.\frac{\partial q(0,t)}{\partial r}\right|_{r=0} = 0 \qquad 2.10$$

$$\left.\frac{\partial C_p}{\partial r}\right|_{r=0} = 0 \qquad 2.11$$

BC 2(A) : At the surface :

Abuzaid (1993) calculated the value of the film resistance for this system to be 1.8E-3 cm^2 / sec. As this value may be considered miniscule, the film resistance contribution may be neglected.

$$-V\frac{dC}{dt} = 4\pi r^2 n \rho_p D_{eff} \cdot \left.\frac{\partial q}{\partial r}\right|_{r=r_s} \qquad 2.12$$

where

$$D_{eff} = \varepsilon \frac{D_p}{\rho_p}\frac{\partial C_p}{\partial q} + D_s \qquad 2.13$$

As

$$\frac{3V_s}{r_s} = 4\pi r_s^2 n \qquad 2.14$$

Therefore

$$V\frac{dC}{dt} = \frac{3V_S}{r_S}\rho_p D_{eff}\left.\frac{\partial q}{\partial r}\right|_{r=r_S} \qquad 2.15$$

BC 2(B)

$$V\frac{dC}{dt} = -W_S\frac{d\bar{q}}{dt} - \varepsilon V_p\frac{d\bar{C}_p}{dt} \qquad 2.16$$

where $\bar{q}$ and $\bar{C}_p$ are average values.

$$V\frac{dC}{dt} = -W_S\frac{d\bar{q}}{dt}\left\{1 + \frac{\varepsilon}{\rho_p}\frac{d\bar{C}_p}{d\bar{q}}\right\} \qquad 2.17$$

$$\bar{q} = \frac{\int_0^{r_s}(4\pi r^2 q)dr}{4\pi r_s^3/3} \qquad 2.18$$

$$\bar{C}_p = \frac{\int_0^{r_s}(4\pi r^2 C_p)dr}{4\pi r_s^3/3} \qquad 2.18b$$

Dimensionless Form

Defining dimensionless variables as :

$$Q = \frac{q}{q_{os}} \quad : \quad \eta = \frac{r}{r_s} \quad : \quad \tau = \frac{D_p t}{r_s^2} \qquad 2.19$$

$$\frac{\partial q}{\partial Q} = q_{os} \;:\; \frac{\partial \tau}{\partial t} = \frac{D_p}{r_s^2} \;:\; \frac{\partial \eta}{\partial r} = \frac{1}{r_s} \qquad 2.20$$

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial Q}\cdot\frac{\partial Q}{\partial \tau}\cdot\frac{\partial \tau}{\partial t} = q_{os}\frac{D_p}{r_s^2}\frac{\partial Q}{\partial \tau} \qquad 2.21$$

$$\frac{\partial q}{\partial r} = \frac{\partial q}{\partial Q}\cdot\frac{\partial Q}{\partial \eta}\cdot\frac{\partial \eta}{\partial r} = \frac{q_{os}}{r_s}\frac{\partial Q}{\partial \eta} \qquad 2.22$$

$$\frac{\partial^2 q}{\partial r^2} = \frac{\partial}{\partial \eta}\cdot\frac{\partial \eta}{\partial r}\left(\frac{q_{os}}{r_s}\cdot\frac{\partial Q}{\partial \eta}\right) = \frac{q_{os}}{r_s^2}\frac{\partial^2 Q}{\partial \eta^2} \qquad 2.23$$

$$\left[\frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q}+1\right]\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left\{\eta^2\left[\frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q}+\frac{D_s}{D_p}\right]\frac{\partial Q}{\partial \eta}\right\} \qquad 2.24$$

The initial condition becomes:

$$\overline{C}(0) = 1$$
$$Q(\eta,0) = 0 \qquad 2.25$$

The boundary conditions become:

B.C.1: At the center of the particle

$$\frac{\partial Q(0,t)}{\partial \eta} = 0 \qquad 2.26$$

B.C.2(A) At the surface of the particle:

$$\frac{d\bar{C}}{d\tau} = 3\alpha \frac{D_{eff}}{D_p}\left[\frac{\partial Q}{\partial \eta}\right]_{\eta=1} \qquad 2.27$$

Define :

$$\alpha = \frac{W_s q_{os}}{VC_o} \qquad 2.28$$

$$\bar{C} = \frac{C(t)}{C_o} \qquad 2.29$$

and

$$\bar{Q} = 3\int_0^1 (Q\eta^2)d\eta = \frac{\bar{q}}{q_{os}} \qquad 2.30$$

Also :

$$\frac{d\bar{q}}{dt} = \frac{d\bar{q}}{d\bar{Q}} \cdot \frac{d\bar{Q}}{d\tau} \cdot \frac{d\tau}{dt}$$

Therefore

$$\frac{d\bar{q}}{dt} = q_{os} \frac{D_p}{r_s^2} \cdot \frac{d\bar{Q}}{d\tau} \qquad 2.31$$

$$\frac{VC_o D_p}{r_s^2}\frac{d\bar{C}}{d\tau} = -W_s \frac{d\bar{q}}{dt}\left\{1 + \frac{\varepsilon}{\rho_p}\frac{d\bar{C}_p}{dq}\bigg|_{avg}\right\} \qquad 2.32$$

Neglecting :

$$\frac{\varepsilon}{\rho_p}\frac{d\bar{C}_p}{dq}\bigg|_{avg} << 1 \qquad 2.33$$

we obtain :

$$\frac{d\bar{C}}{d\tau} = -\left(\frac{q_{OS} W_S}{VC_O}\right).\frac{d\bar{Q}}{d\tau} \qquad 2.34$$

$$\frac{d\bar{C}}{d\tau} = -\alpha.\frac{d\bar{Q}}{d\tau} \qquad 2.35$$

Integrating this boundary conditions yields:

$$\bar{C}(\tau)=1 - \alpha\left[\bar{Q}(\tau) - \bar{Q}(\tau=0)\right] \qquad 2.36$$

Conducting an adsorbate balance at any time t in the system yields

$$VC_o = VC_t + W_s\bar{q} \qquad 2.37$$

$$\bar{q} = \frac{V}{W_s}(C_o - C_t) \qquad 2.38$$

At equilibrium we have :

$$VC_o = VC_\infty + W_s\bar{q}_\infty \qquad 2.39$$

$$\bar{q}_\infty = \frac{V}{W_s}(C_o - C_\infty) \qquad 2.40$$

$$\frac{\bar{q}_\infty}{\bar{q}_o} = \frac{VC_o}{W_s\, q_{os}}\left(1 - \frac{C_\infty}{C_o}\right) \;;\quad \bar{q}_o = q_{os} \qquad 2.41$$

Hence :

$$\alpha = \frac{W_s q_{os}}{VC_o} = \left(1 - \frac{C_\infty}{C_o}\right) / \frac{\bar{q}_\infty}{\bar{q}_o} \qquad 2.42$$

Also

$$\frac{\bar{q}}{\bar{q}_\infty} = \frac{M_t}{M_\infty} = \frac{[C_o - C_t]}{[C_o - C_\infty]} = \frac{[1 - C_t / C_o]}{[1 - C_\infty / C_o]} \qquad 2.43$$

where $\frac{M_t}{M_\infty}$ is the fractional uptake at any time. It is an indication of the proximity to equilibrium.

$$1 - \frac{M_t}{M_\infty} = 1 - \frac{[1 - C_t/C_o]}{[1 - C_\infty/C_o]} \qquad 2.44$$

2.3.2. Taking into Account the Concentration Dependence of Surface Diffusivity.

At high concentration levels in an adsorbent, the equilibrium isotherm becomes non-linear so that the gradient in concentration is no longer the same as the gradient in chemical potential. By considering the relationship between chemical potential and gradient one obtains Darken's relation.

$$D_s = D_{so}\left(\frac{d\ln C}{d\ln q}\right)_T \qquad 2.45$$

Darken's relation can be derived for various isotherm models and this is done in Table 2.1. We observe, that except for the Freundlich isotherm, the diffusivity is strongly concentration dependent for all other isotherms. The

$$D_s = D_{so}\left(\frac{d\ln C}{d\ln q}\right)_T \qquad 2.45$$

Darken's relation can be derived for various isotherm models and this is done in Table 2.1. We observe, that except for the Freundlich isotherm, the diffusivity is strongly concentration dependent for all other isotherms. The observation with regard to the Freundlich isotherm was recently reported by Gutsche and Yoshida (1994). They also reported that it was not able to reflect the concentration dependence of their data. Also Hu et al., (1994) corroborated this fact by their extensive theoretical and experimental studies of the intrinsic concentration dependence of surface diffusivity in hydrocarbons and granular activated carbon systems. Garg and Ruthven(1972) used the Darken relationship in explaining the concentration dependence of diffusivity in zeolites using the Langmuir and Volmer isotherms.

2.3.3 Effective Pore Volume Diffusivity Coefficient.

The effective pore volume diffusivity coefficient was estimated using the relation:

$$D_{e,p} = \frac{D_{AB}}{\tau_p} \qquad 2.46$$

where D_{AB}, is the molecular diffusivity and τ_p is the tortuosity factor. The value of τ_p for activated carbon is reported to be 3.5 (Leyva-Ramos and Geankoplis, 1994) and this is in good agreement with the general values reported earlier in the literature (Komiyama and Smith, 1974; Shibuya and Kawazoe, 1978). The value of D_{AB} predicted from correlations was reported

Table 2.1 : Normalized Values Of $d\ln C/d\ln q$ For Various Isotherms

ISOTHERM FORM		$\frac{d\ln C}{d\ln q}$	
NAME	**EQUATION**	**θ – FORM**	**λ – FORM**
Henry's Isotherm	$q = K_{HI}C$	1	1
Langmuir Isotherm	$\frac{q}{q_s} = \frac{K_L C}{1+K_L C}$	$\frac{1}{1-\theta}$	$\frac{1}{1-\lambda Q}$
Toth Isotherm	$\frac{q}{q_s} = \frac{K_T C}{\left[1+(K_T C)^n\right]^{1/n}}$	$\frac{1}{1-\theta^n}$	$\frac{1}{1-(\lambda Q)^n}$
Freundlich Isotherm	$q = K_F C^{\frac{1}{n}}$	n	n
Langmuir-Freundlich Isotherm	$\frac{q}{q_s} = \frac{K_{LF} C^{1/n}}{1+K_{LF} C^{1/n}}$	$\frac{n}{1-\theta}$	$\frac{n}{1-\lambda Q}$
Volmer's Isotherm	$C = b\left(\frac{\theta}{1-\theta}\right)\exp\left(\frac{\theta}{1-\theta}\right)$	$\frac{1}{(1-\theta)^2}$	$\frac{1}{(1-\lambda Q)^2}$
Virial Isotherm	$C = \frac{q}{K}\exp(A_1 q + A_2 q^2 + A_3 q^3 + \ldots.)$	$1+\sum_{i=1}^{n} A_i^* \theta^i$ Where $A_i^* = iA_i$	$1+\sum_{i=1}^{n} A_i^* (\lambda Q)^i$ Where $A_i^* = iA_i$
Myer's Isotherm	$C = \frac{q}{K_H}\exp(Kq^a)$	$1 + K^* Q^a$ *where* $k^* = akq_S^a$	$1 + K^* \lambda^a Q^a$ where $k = akq_s^a$

directly. from the Wilke-Chang equation (Reid et al., 1977). The molal volume of o-cresol (Hydroxylmethylbenzene, $CH_3-C_6H_4-OH$) was estimated from the LeBas Atomic Volumes method (Reid et al., 1977).

$$D_{AB} = \frac{7.4E-8(\xi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \qquad 2.47$$

2.3.4 Langmuir Freundlich Isotherm.

The general form of Langmuir Freundlich isotherm is :

$$\theta = \frac{q}{q_s} = \frac{k_{LF} C^{1/n}}{1 + k_{LF} C^{1/n}} \qquad 2.48$$

The following can readily be obtained by differentiation.

$$\frac{\partial C_p}{\partial q} = \frac{n}{k_{LF}^n q_s} \frac{(Q\lambda)^{n-1}}{(1-Q\lambda)^{n+1}} \qquad 2.49$$

Defining :

$$\lambda = \frac{q_o}{q_s} = \frac{k_{LF} C_o^{1/n}}{1 + k_{LF} C_o^{1/n}} \qquad 2.50$$

In dimensionless form we have :

$$\lambda Q = \frac{q}{q_s} = \frac{k_{LF} (\bar{C} C_o)^{1/n}}{1 + k_{LF} (\bar{C} C_o)^{1/n}} \qquad 2.51$$

$$\lambda Q_\infty = \frac{q_\infty}{q_s} = \frac{k_{LF}\left(\overline{C}_\infty C_o\right)^{1/n}}{1 + k_{LF}\left(\overline{C}_\infty C_o\right)^{1/n}} \qquad 2.52$$

The overall equation (2.24) then becomes :

$$\left[\frac{\varepsilon}{\rho_p}\frac{n}{k_{LF}^n}\frac{(Q\lambda)^{n-1}}{q_S(1-Q\lambda)^{n+1}} + 1\right]\frac{\partial Q}{\partial \tau} =$$
$$\frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left\{\eta^2\left[\frac{\varepsilon}{\rho_p}\frac{n}{k_{LF}^n}\frac{(Q\lambda)^{n-1}}{q_S(1-Q\lambda)^{n+1}} + \frac{D_S}{D_p}\frac{n}{(1-Q\lambda)}\right]\frac{\partial Q}{\partial \eta}\right\} \qquad 2.53$$

As

$$\frac{\varepsilon}{\rho_p}\frac{n}{k_{LF}^n}\frac{(Q\lambda)^{n-1}}{q_S(1-Q\lambda)^{n+1}} << 1 \qquad 2.54$$

The left hand bracketed side of equation (2.53) may be set equal to 1. Therefore, the final equation becomes :

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left\{\eta^2\left[\frac{\varepsilon}{\rho_p}\frac{n}{k_{LF}^n}\frac{(Q\lambda)^{n-1}}{q_S(1-Q\lambda)^{n+1}} + \frac{D_S}{D_p}\frac{n}{(1-Q\lambda)}\right]\frac{\partial Q}{\partial \eta}\right\} \qquad 2.55$$

This must be solved numerically together with initial condition and the boundary conditions equations 2.25, 2.27, and 2.36.

2.4 Results And Discussion

In order to ascertain the most efficient mechanism for this work, five different models are examined, namely

Model 1 : The pore diffusion model,

Model 2 : The homogeneous surface diffusion model with constant surface diffusivity coefficient,

Model 3 : The homogeneous surface diffusion model with concentration dependent surface diffusivity coefficient,

Model 4 : The pore and surface diffusion model with constant surface diffusivity coefficient, and

Model 5 : The pore and surface diffusion model with concentration dependent surface diffusivity coefficient.

In models 3 and 5, the dependence of surface diffusivity on solid phase concentration was accounted for by taking chemical potential as the driving force using the Darken's relation. The equation data for phenol and o-cresol adsorption on GAC was fitted using a nonlinear regression program. The fit of the model to the data is illustrated in Figures 2.1 and 2.2, and the parameters of the isotherm are giving in Table 2.2. Abuzaid (1993) fitted the data using the Freundlich model but as this isotherm does not provide any indication of the saturation loading, the Langmuir Freundlich model was employed. The saturation concentration for phenol appears reasonable at 0.25 mg/mg but that for o-cresol appears high at 0.6 mg/mg.

The implicit Crank - Nicolson finite difference scheme was used to solve the resulting equations. This method averages the forward and backward

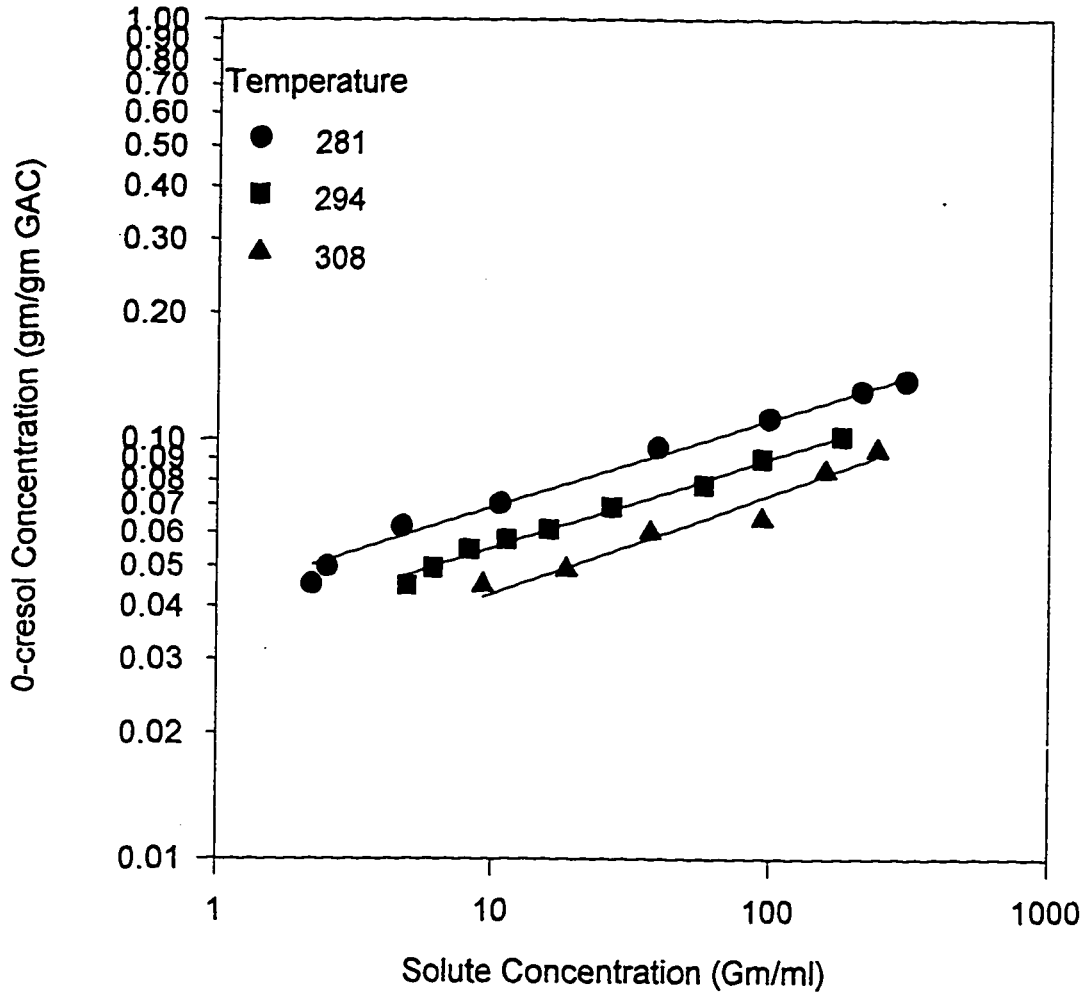


Figure 2.1. Langmuir-Freundlich fit of phenol adsorption on GAC

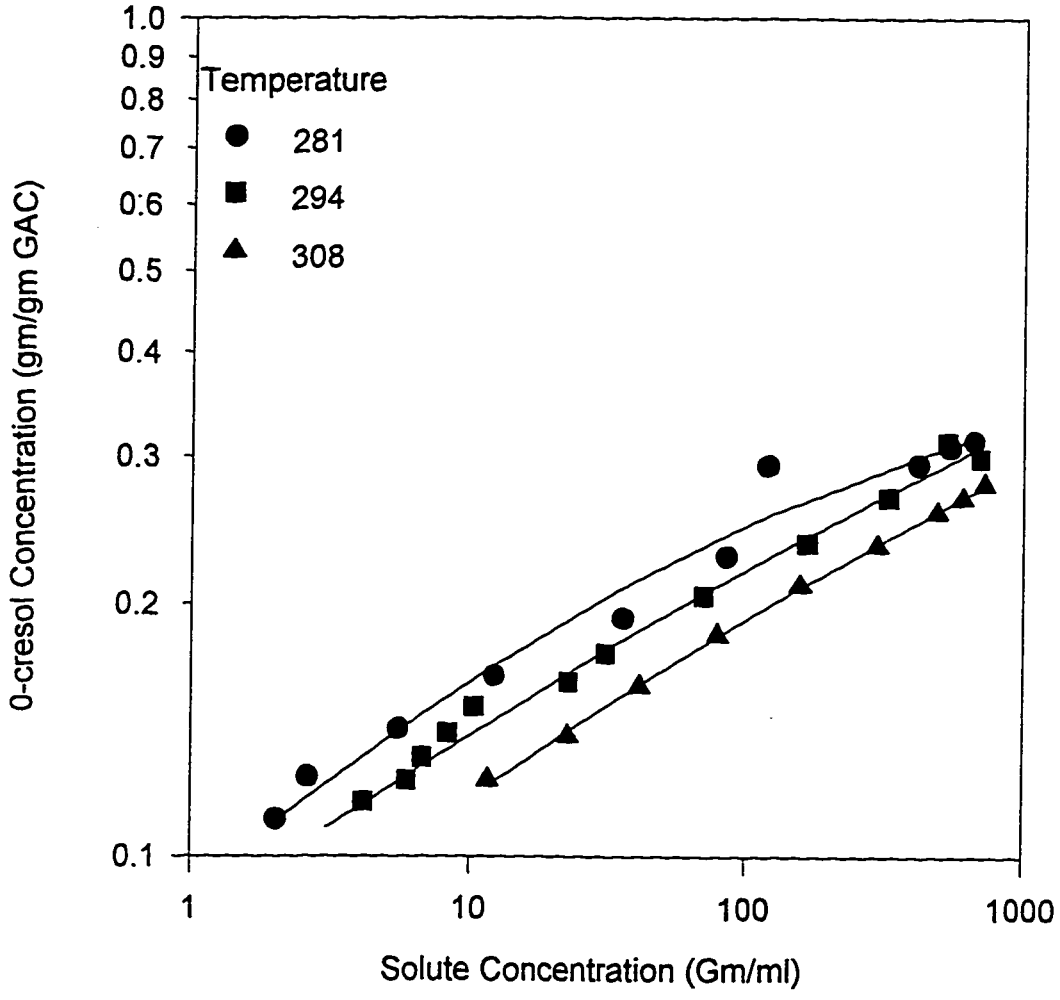


Figure 2.2. Langmuir-Freundlich fit of o-cresol adsorption on GAC

Table 2.2 : Input Parameters For Optimization of Surface Diffusivity

1	2	3	4	5			6	7
Temp, (K)	C_O, mg / L	C_∞ / C	Pore Fraction	Isotherm Constant			Pore Diffusi -vity Coeff.	Particle Density, ρ_p, mg / cm^3
				k_{LF}, (mg / L)	n	q_s, mg / m	D_p * E10 m^2 / s	
For phenol.								
281	1000	0.213	0.63	0.1873	3.125	0.25	1.3957	0.67
294	1000	0.261	0.63	0.1345	3.125	0.25	2.0742	0.67
308	1000	0.463	0.63	0.0975	3.125	0.25	2.9610	0.67
For o-cresol								
281	1000	0.252	0.63	0.1842	3.448	0.60	1.6059	0.67
294	1000	0.301	0.63	0.1353	3.448	0.60	2.3865	0.67
308	1000	0.347	0.63	0.1230	3.448	0.60	3.4069	0.67

finite differences and is unconditionally stable. The resulting tridiagonal matrices were solved using Thomas algorithm. The applicability of the program was tested by reproducing the results of Suzuki (1980) for constant surface diffusivity and Freundlich isotherm (see Figure 2.3). The time step and number of nodes used are respectively 0.0005 and 51. A comparison of the results of the program for 21 nodes and 71 nodes is presented in Figure 2.4. The two results are indistinguishable. This is an attestation of the accuracy of the program used.

The IMSL library optimization program (BCPOL) was used in this work to minimize the sum of the root mean squares (rms.) of the residuals between predicted and experimental concentration values. The two forms of rms. equations commonly used are :

$$\text{(i) The normalized RMS} = 100 * \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{C_{i,exp} - C_{i,cal}}{C_{i,exp}}\right)} \qquad 2.56$$

$$\text{(ii) The non-normalized RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(C_{i,exp} - C_{i,cal}\right.} \qquad 2.57$$

The normalized RMS. was used in this work. The model parameter determined from the optimization program is the surface diffusivity coefficient at zero concentration.. The input parameters for the various models are given in Table 2.2. The parameters used by the various models are :

Model 1 input : Columns 2 - 7

Model 2 input : Columns 2, 3, and 5

Model 3 input : Columns 2, 3, and 5

Model 4 input : Columns 2 - 7

Model 5 input : Columns 2 - 7

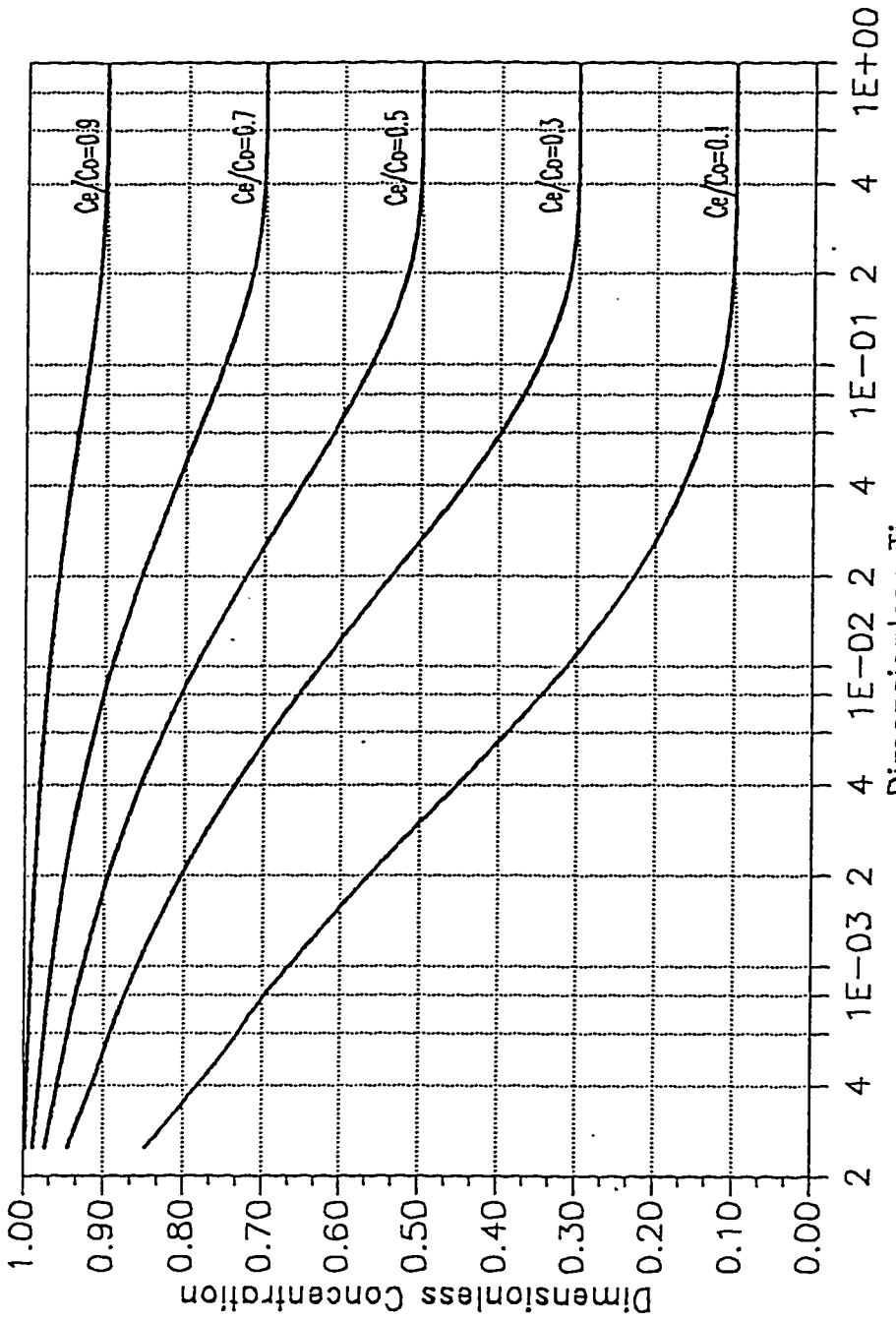


Fig 2.3: Reproducibility of Program to Produce data of Suzuki (1990), (Page 9).

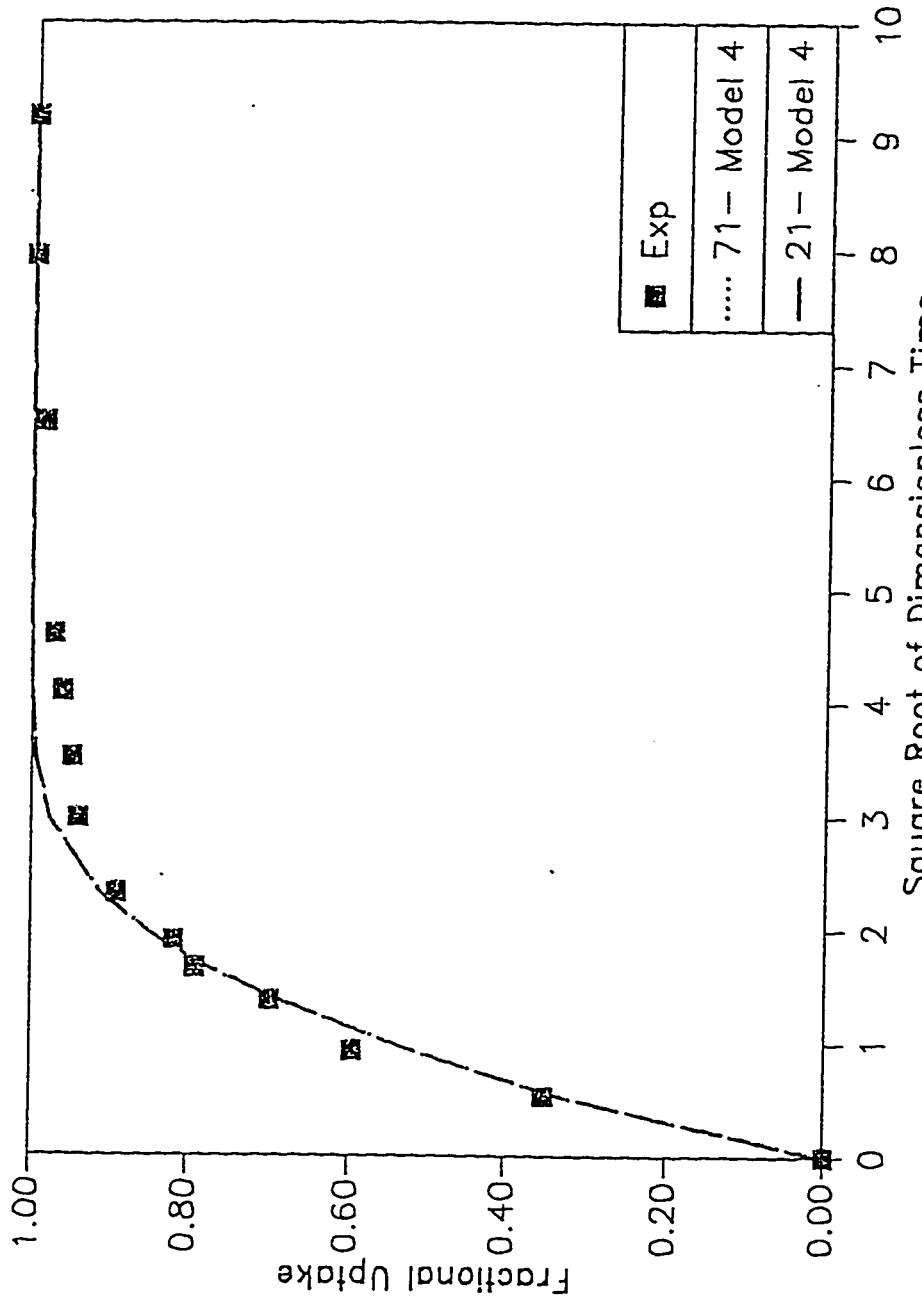


Fig 2.4: Predicted and Experimental Fractional Uptake at 308K. Adsorption of phenol. Comparison Between 71 and 21 nodes

To assess the effectiveness of each model, the root mean square deviations of the predicted concentration decay from the experimental values were computed. These are given in Table 2.2. The plots of the various models are presented in Figures 2.5 to 2.10. Note, $\varepsilon = 0.64$ for the GAC used.

The pore diffusion model gave very poor fits with large rms. values. This indicates that the dominant mechanism in the adsorption process is not pore diffusion. Pore diffusion alone is inadequate in predicting the adsorption of phenol on granular activated carbon (GAC) when you have a high concentration data. However, Leyva and Geankoplis (1994) successfully fitted their data for phenol - GAC system using pore diffusion model. This is because their data is of very low concentration (< 50 mg/L) which should be compared to the data used in this work which is at a high concentration (1000 mg/L). The poor fits of the pore diffusion model are shown in Figures 2.5 to 2.7.

The homogeneous surface diffusion model with constant D_s gives reasonably good fits as may be seen in Figures 2.5 to 2.7. This indicates that the surface diffusion model can be used in predicting the adsorption process. Abuzaid fitted this data using Freundlich isotherm and HSDM. and obtained reasonable fits at 281K, 294K and 308K. The difference in fits and resulting surface diffusivity coefficients values between this work and Abuzaid's may be partly attributed to the different isotherm forms used. The Freundlich isotherm gave a better fit than the Langmuir Freundlich isotherm. However, the surface diffusivity coefficients obtained are well within the range reported in literature as may be seen in Tables 2.3 and 2.4. The model which assumed a constant surface diffusivity coefficient exhibits a rather strong

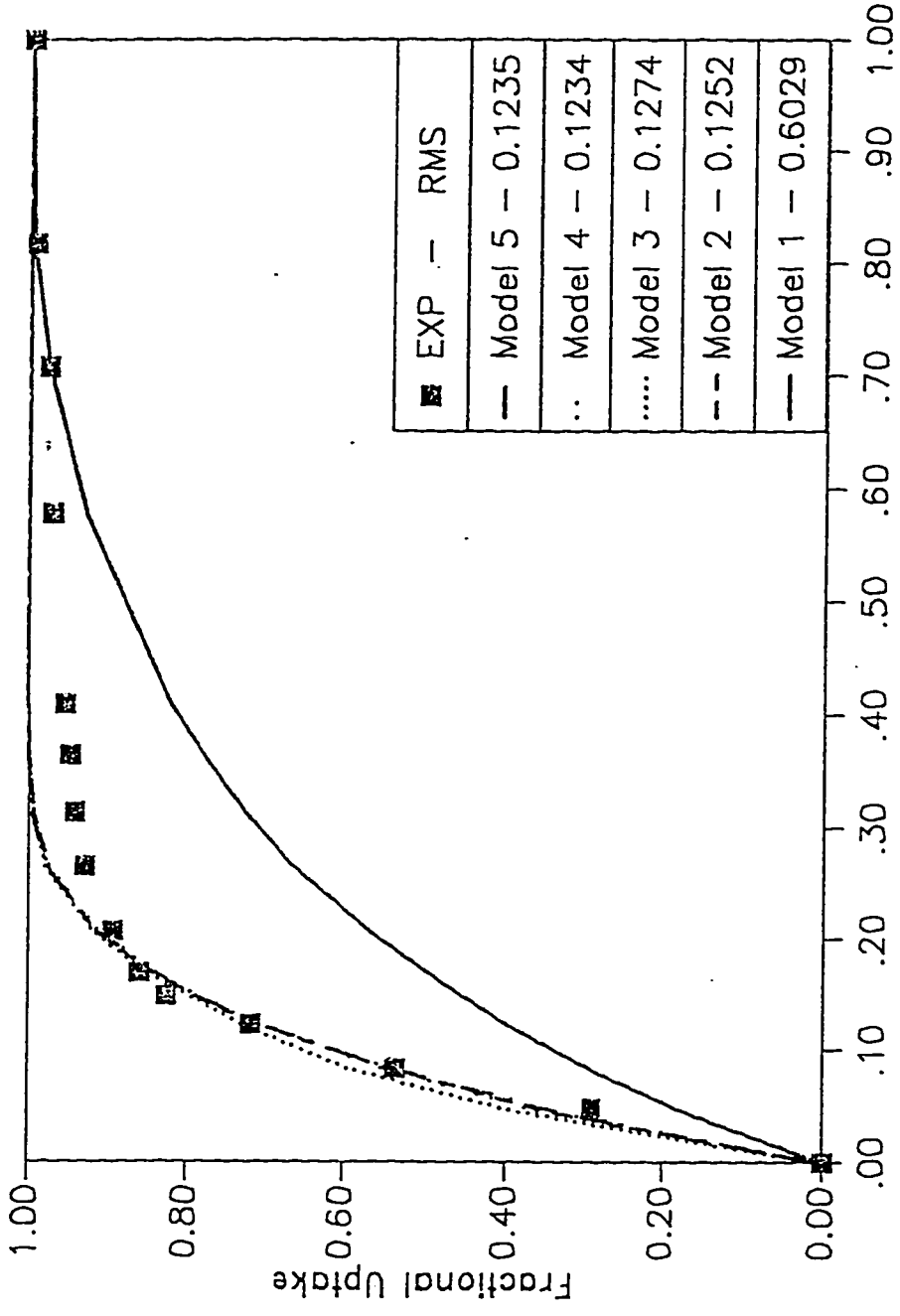


Fig. 2.5: Predicted and Experimental Uptake at 281K. Adsorption of phenol

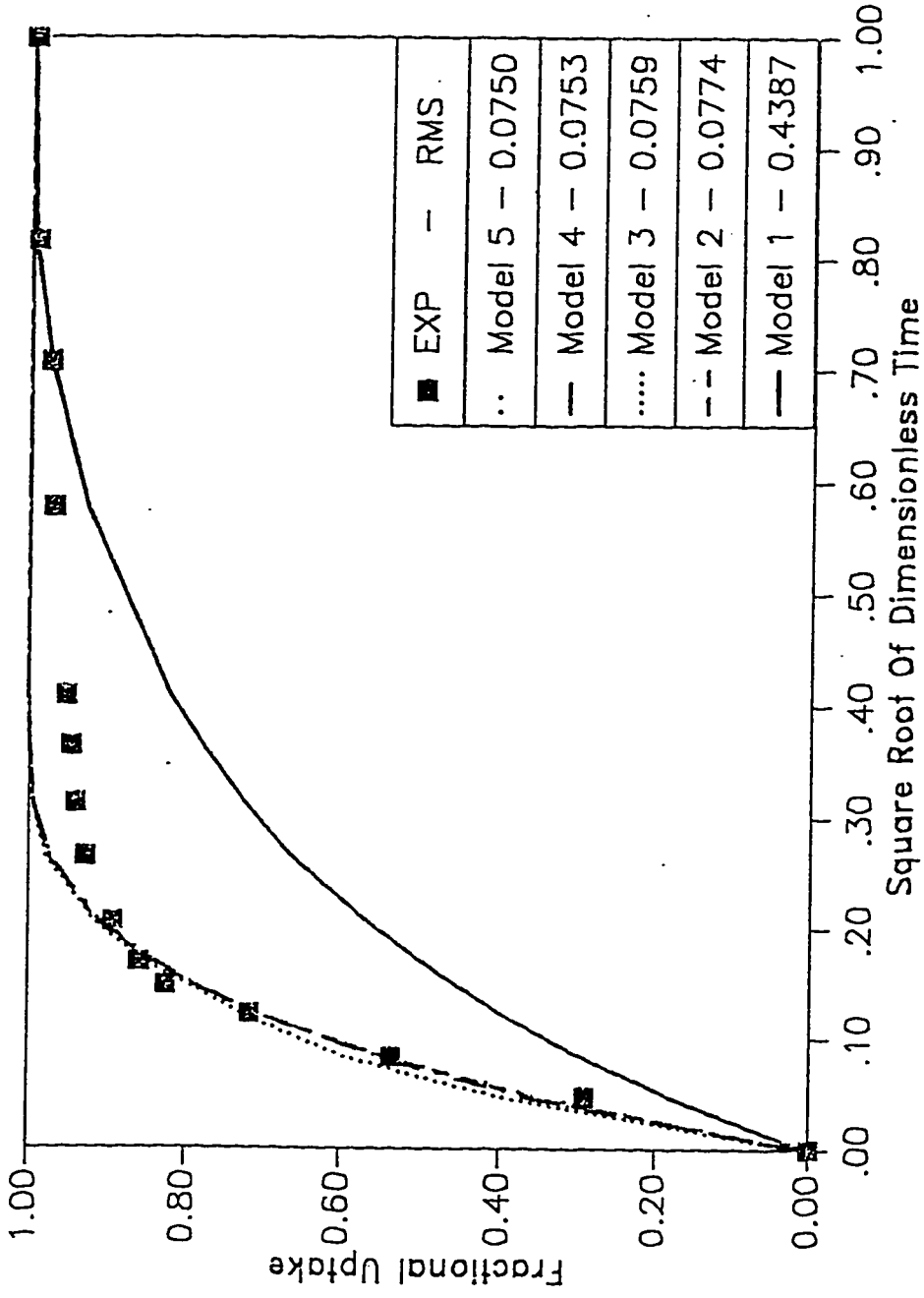


Fig. 2.6: Predicted and Experimental Uptake at 294K. Adsorption of phenol.

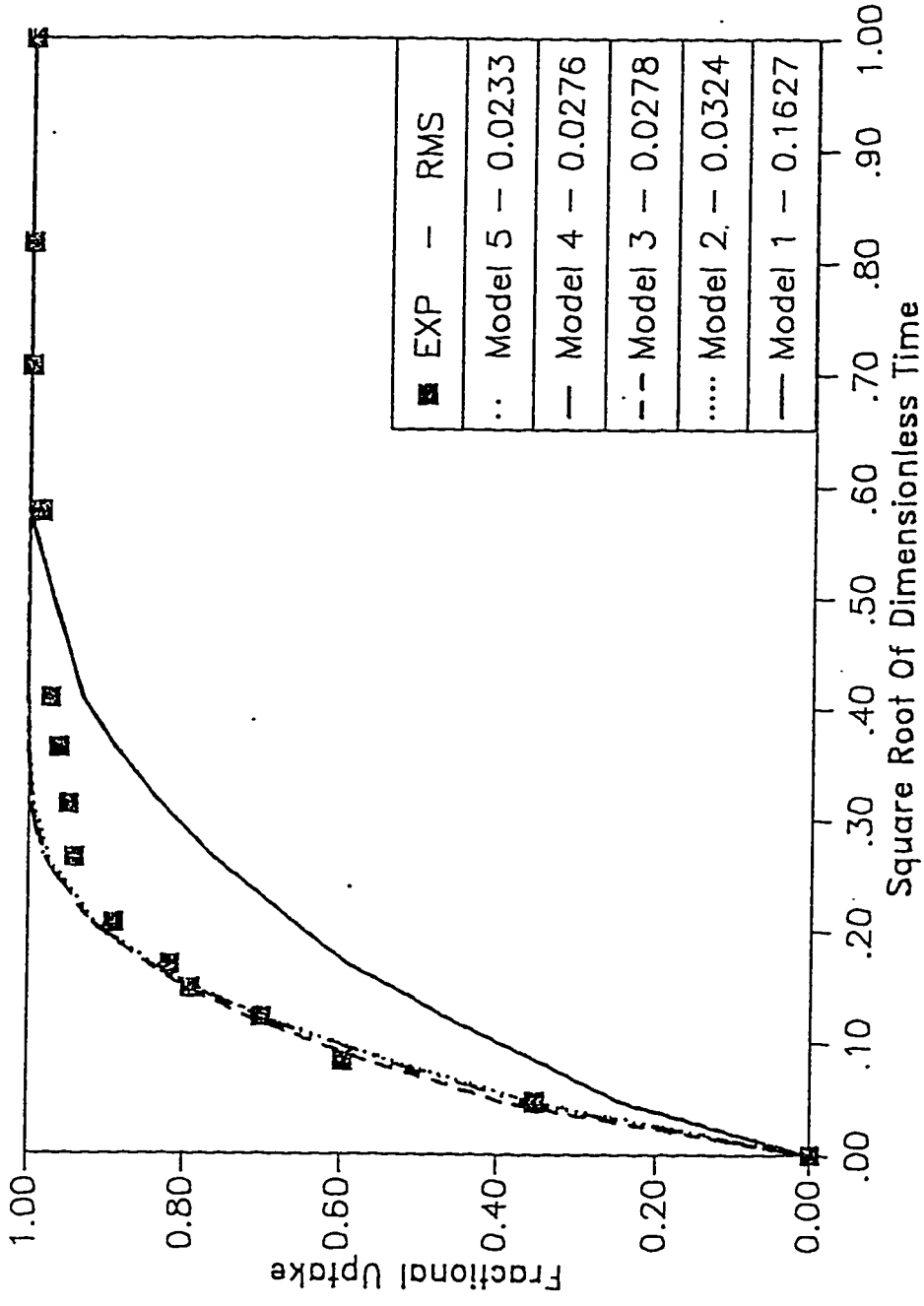


Fig 2.7: Predicted and Fractional Uptake at 308K. Adsorption of phenol

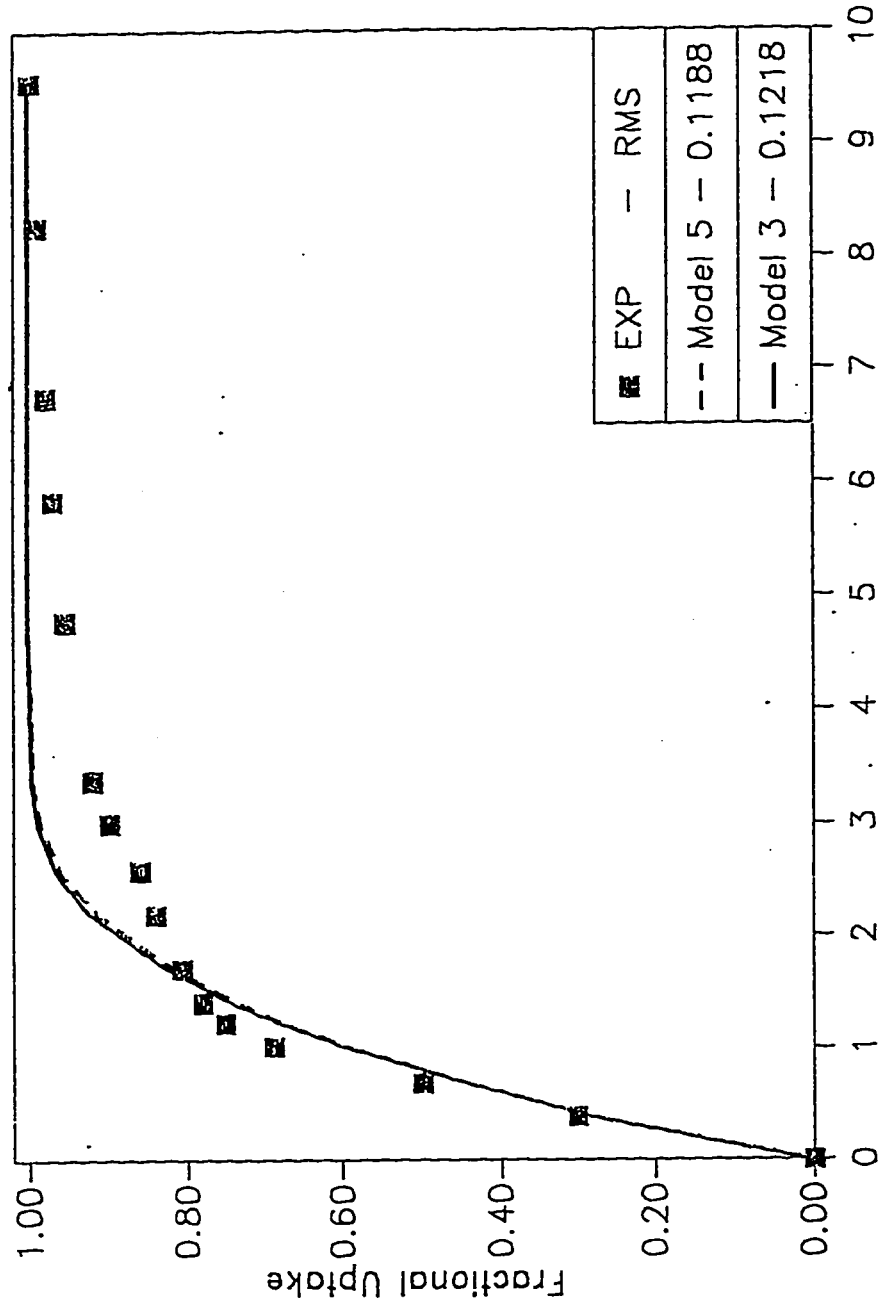


Fig. 2.8: Predicted and Experimental Fractional Uptake at 281K. Adsorption of o-Cresol

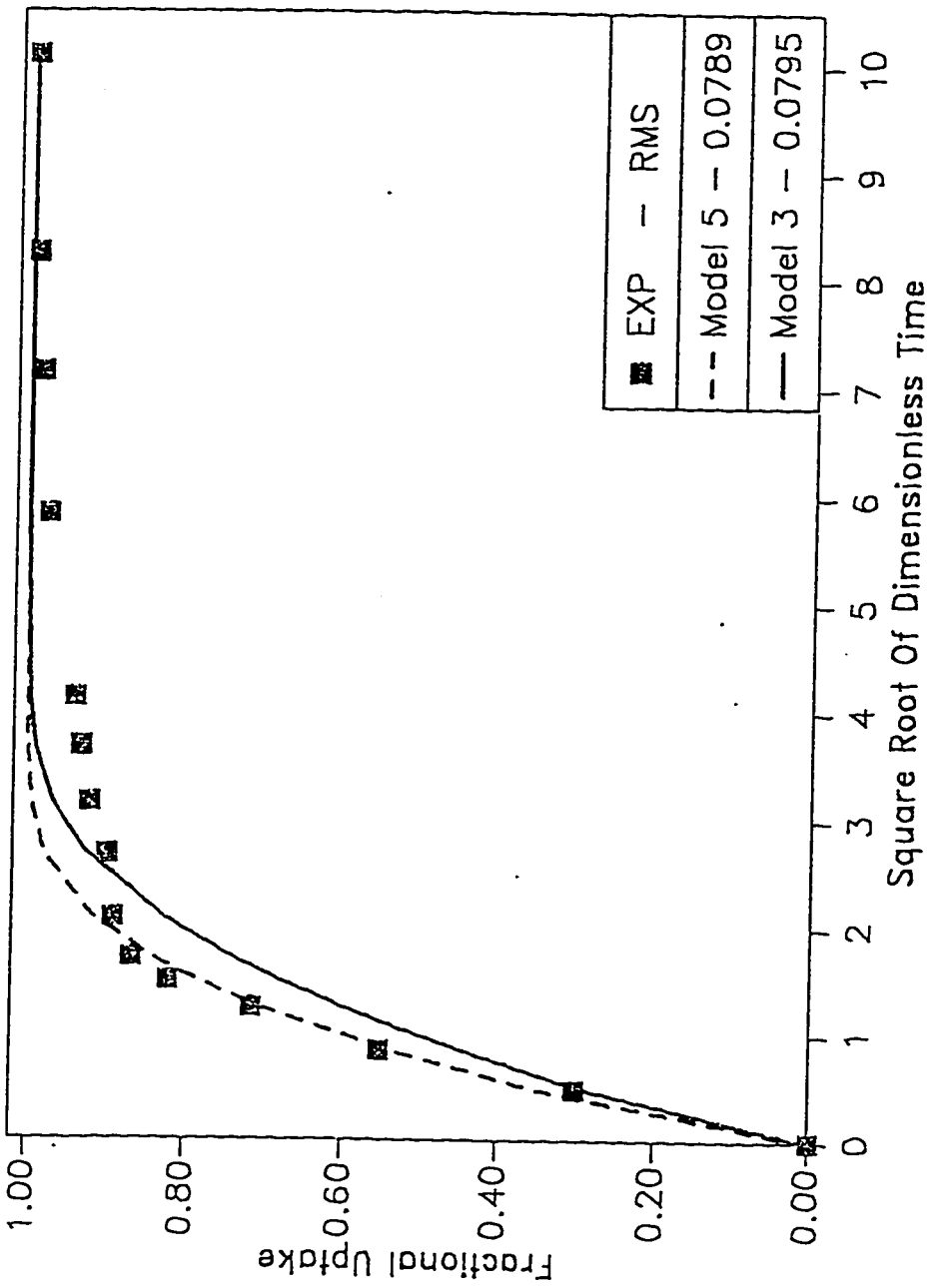


Fig. 2.9: Predicted and Experimental Fractional Uptake at 294K. Adsorption of o-Cresol

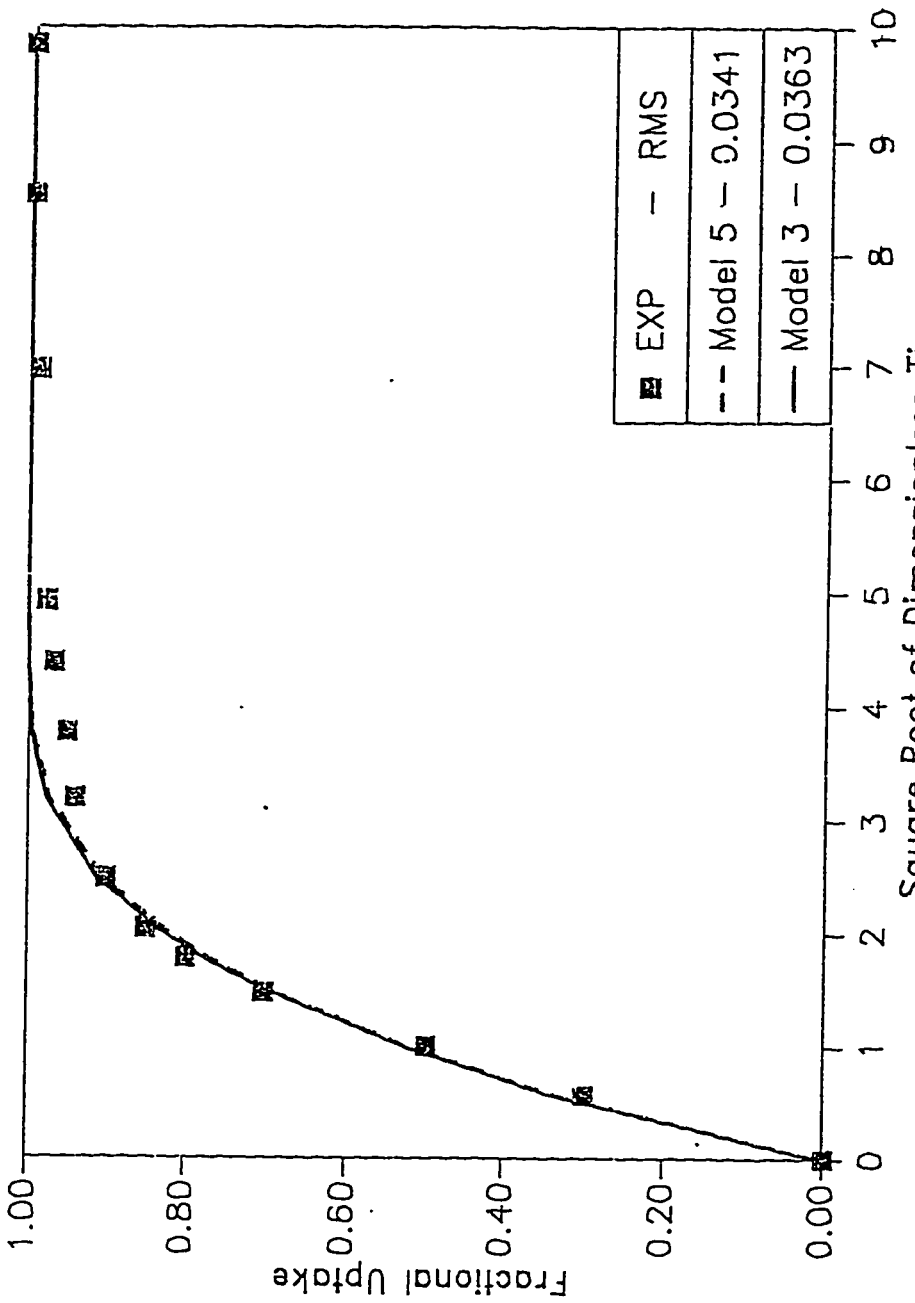


Fig 2.10: Predicted and Experimental Fractional Uptake at 308K. Adsorption of o-Cresol.

Table 2.3 : Diffusivity Coefficient And RMS values For The Various Models.

Temp (K)	Pore Diffusion Model (PD)		Homogeneous Surface Diffusion Model (HSDM) with constant surface Diffusivity		Homogeneous Surface Diffusion Model (HSDM) With concentration Dependent surface Diffusivity.		Pore And Surface Diffusion Model (PSD) with constant surface Diffusivity		Pore And Surface Diffusion Model (PSD) With concentration Dependent Surface Diffusivity	
	$D_p * E10$ (m^2/s)	RMS.	$D_s * E12$ (m^2/s)	RMS.	$D_{so} * E12$ (m^2/s)	RMS.	$D_s * E12$ (m^2/s)	RMS.	$D_{so} * E12$ (m^2/s)	RMS.
For phenol										
281	1.396	60.29	6.16	12.52	1.12	12.74	5.17	12.34	0.82	12.35
294	2.074	43.87	7.97	7.74	1.61	7.59	6.29	7.53	1.33	7.50
308	2.961	16.27	9.05	3.24	1.95	2.78	5.92	2.76	1.30	2.33
For o-cresol										
281	1.606				1.0	12.18			0.803	11.88
294	2.387				1.735	7.96			1.468	7.90
308	3.407				1.745	3.63			1.346	3.65

Table 2.4 : Surface Diffusivity Coefficients from Literature for Batch Data and HSDM Model.

Researcher	Temp	Phenol D_s Values		o-cresol D_s Values	
	K	D_s*E12 (m^2/s)	C_o, mg/L	D_s*E12 (m^2/s)	C_o, mg/L
Suzuki and Kawazoe (1975)	room	4.3	-	-	-
Vidic and Suidan (1992)	308	-	-	2.406	1000.0
Vidic et al. (1994)	294	2.5893 4.756 10.728	100.0 200.0 800.0	-	-
Crittenden and Weber (1978)	room	3.53	465.0	-	-
Matthew and Su(1983)	297	3.75	100.0	-	-
Abuzaid (1993)	281 294 308	4.9 6.3 8.8	1000.0	8.3	1000.0

dependence of diffusivity on the solid surface concentration from point to point. Consequently, a substantial variation in the values of the surface diffusivity coefficient with time was observed suggesting the need to use a concentration dependent diffusivity model to account for this dependence. Hence Darken's relation was incorporated into the constant surface diffusivity coefficient model. The degree of fit obtained with the concentration dependent surface diffusivity model was slightly better than that obtained from its constant diffusivity counterpart. Moreover, this modification exerted a marked degree of influence on the variation of the surface diffusivity coefficient with time. There was a substantial reduction in variation but it was still not eliminated as may be observed in Figure 2.11. Darken's relation appreciably accounted for the concentration dependence of surface diffusivity coefficient with time. This observation is contrary to those of Hu et al. (1994), and Gutsche and Yoshida (1994). These researchers reported that the Darken's relation could only slightly account for the concentration dependence.

The dual mechanism pore and surface diffusion model (PSD) was used in order to access the importance of pore diffusion contribution to the adsorption process. The PSD model was also used by Hu et al. (1994) and, Leyva and Geankoplis, (1994). The fits obtained from the PSD models were only slightly better than those obtained from the surface diffusion models as may be seen in Figure 2.5 to 2.10. Thus when high concentration data are fitted, the HSDM and the PSD model can predict the adsorption process equally well. The rms. values were in the range of 2.0 -13.5. Notably, the variation in the value of the surface diffusivity coefficient with time in the PSD model was markedly reduced when concentration dependence was accounted for as may be observed in Figure 2.12. Also, the fits from the

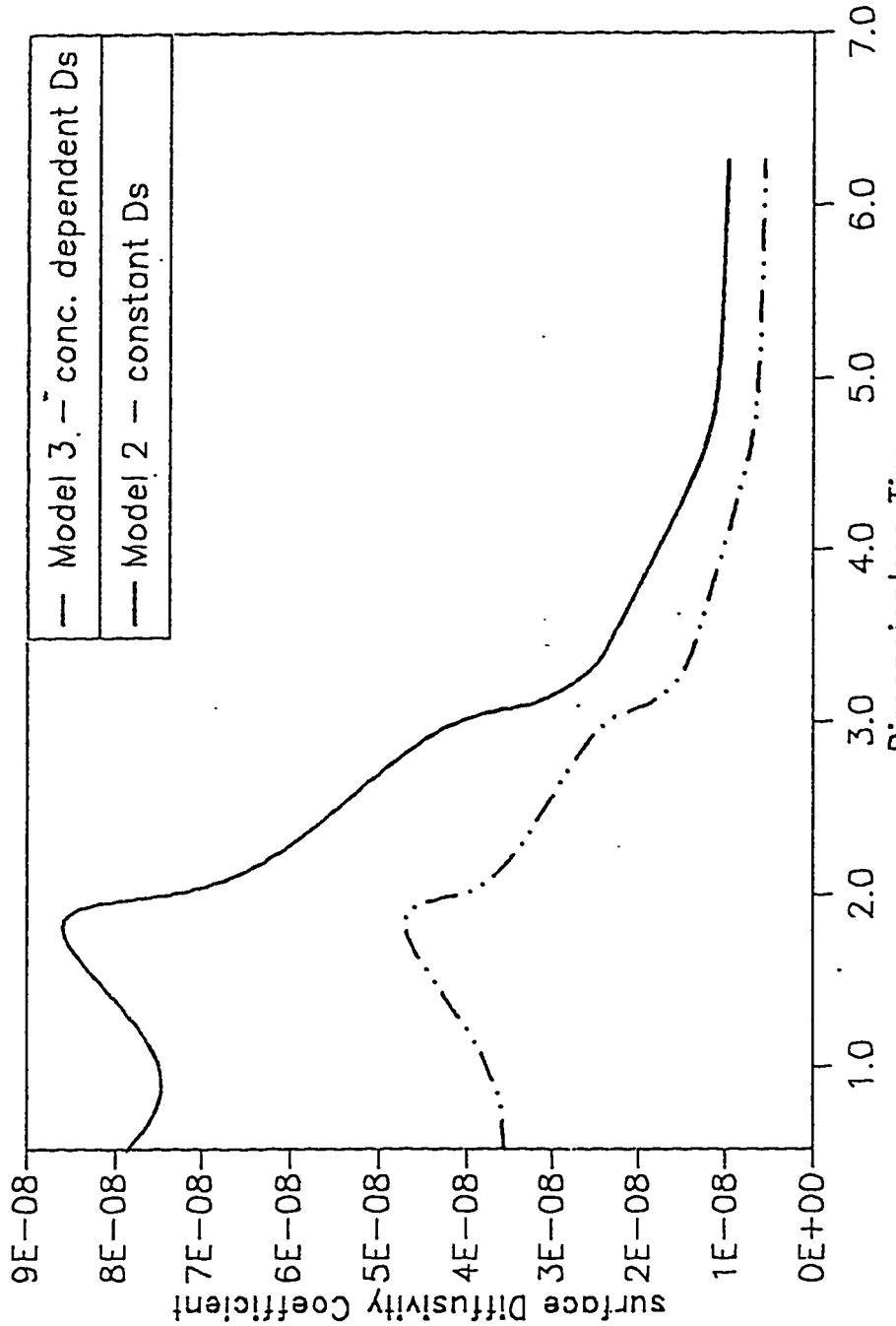


Fig 2.11 : Plot of Ds Vs Dimensionless Time at 281K.
Adsorption of phenol. Comparison between model 2 and 3

constant surface diffusivity coefficient model were almost identical to those from the concentration dependent diffusivity counterpart; the former being slightly better. The slight difference is attributed to noise in the program and to the fact that part of the resistance is being accounted for by pore diffusion.

The D_s values obtained are within the range of the values reported in the literature for both phenol and o-cresol as may be seen in Tables 2.3 and 2.4. The D_s values from the HSDM are higher than those from the PSD. This is expected as part of the diffusion flux is accounted for by pore diffusion in the PSD model. The D_s values increases with temperature continually in the case of the HSDM model. This is consistent with theory as physical adsorption is an exothermic phenomena. In the PSD model however, the D_s increases for the first two temperatures and then decreases at the third temperature. This seeming anomaly is accounted for by the rapid increase in the value of D_p with temperature. As temperature increases, the contribution of pore diffusion increases rapidly as the D_p value increases. Hence an increasing proportion of the diffusion flux is being accounted for by pore diffusion resulting in lower contribution by surface diffusion and as a result a decrease in D_s value. It worth noting that the variation in the D_s from the PSD model is very small compared to that from the HSDM. This observation is again attributed to the pore diffusion contribution which is not accounted for in the HSDM but is accounted for in the PSD model.

Surface adsorption is an activated process and hence D_s is a function of temperature. The D_{s0} values obtained in this study increases with temperature. This is a general observation. A plot of the logarithm of D_{s0} versus the inverse of temperature 1/T gives a straight line. These plots are shown for phenol and o-cresol in Figures 2.13 to 2.16. The temperature dependenceof D_{s0} is expressed as

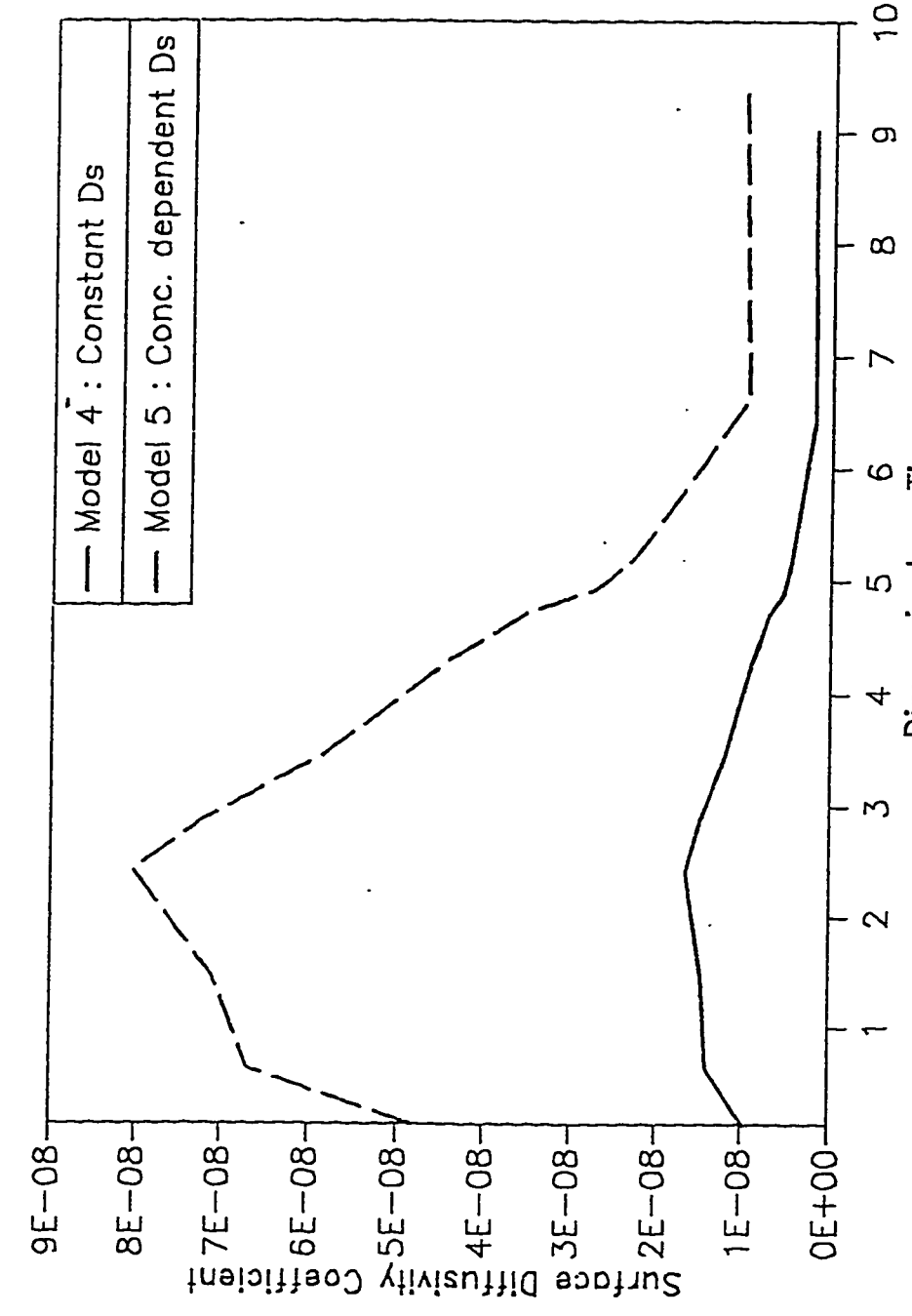


Fig. 2.12 Plot of Ds vs. Dimensionless Time at 294 K.
Adsorption of Phenol (Comparison between models 4 & 5)

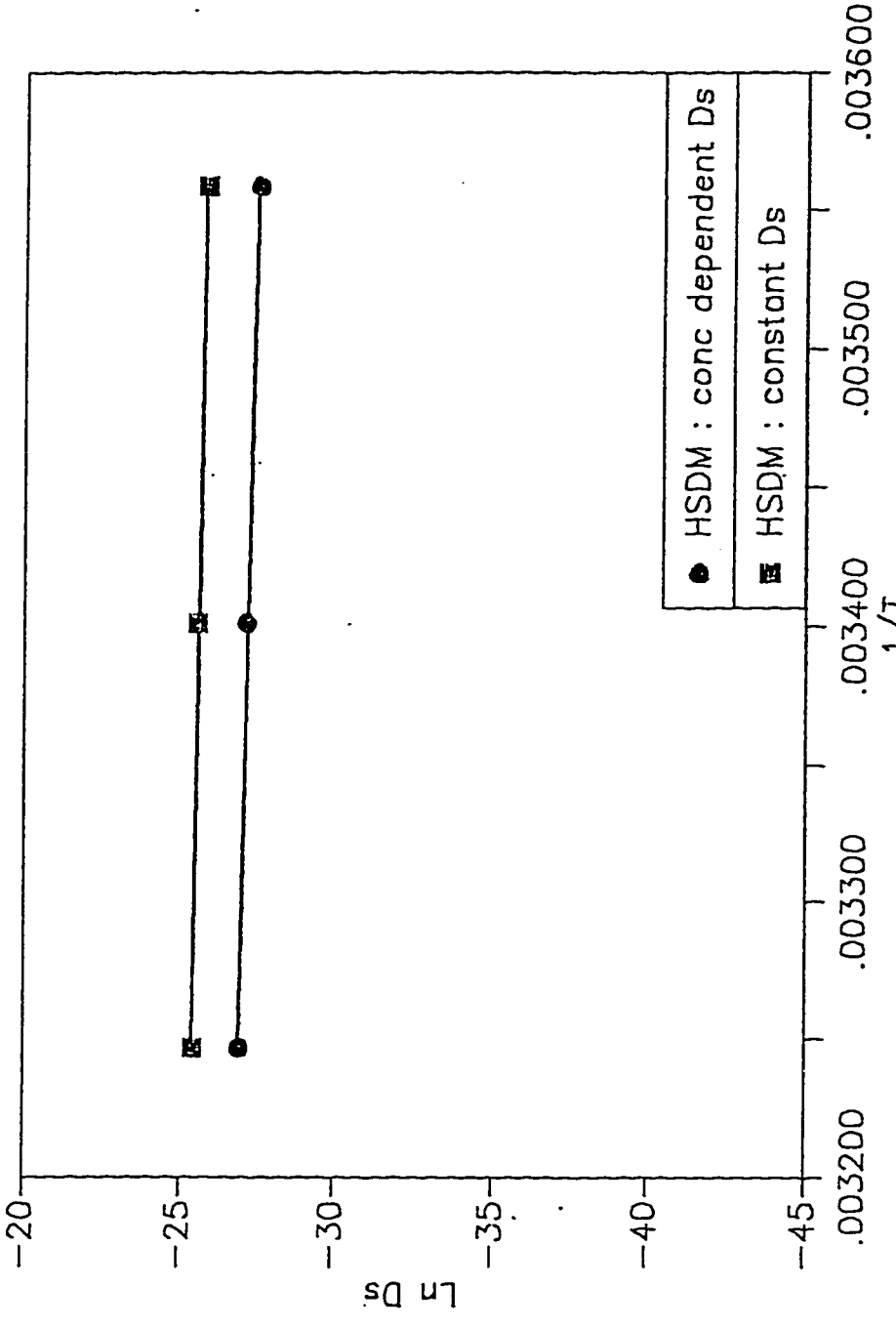


Fig 2.13: Plot of Ln Ds Vs 1/T
HSDM – Model 2 and 3. Adsorption of phenol

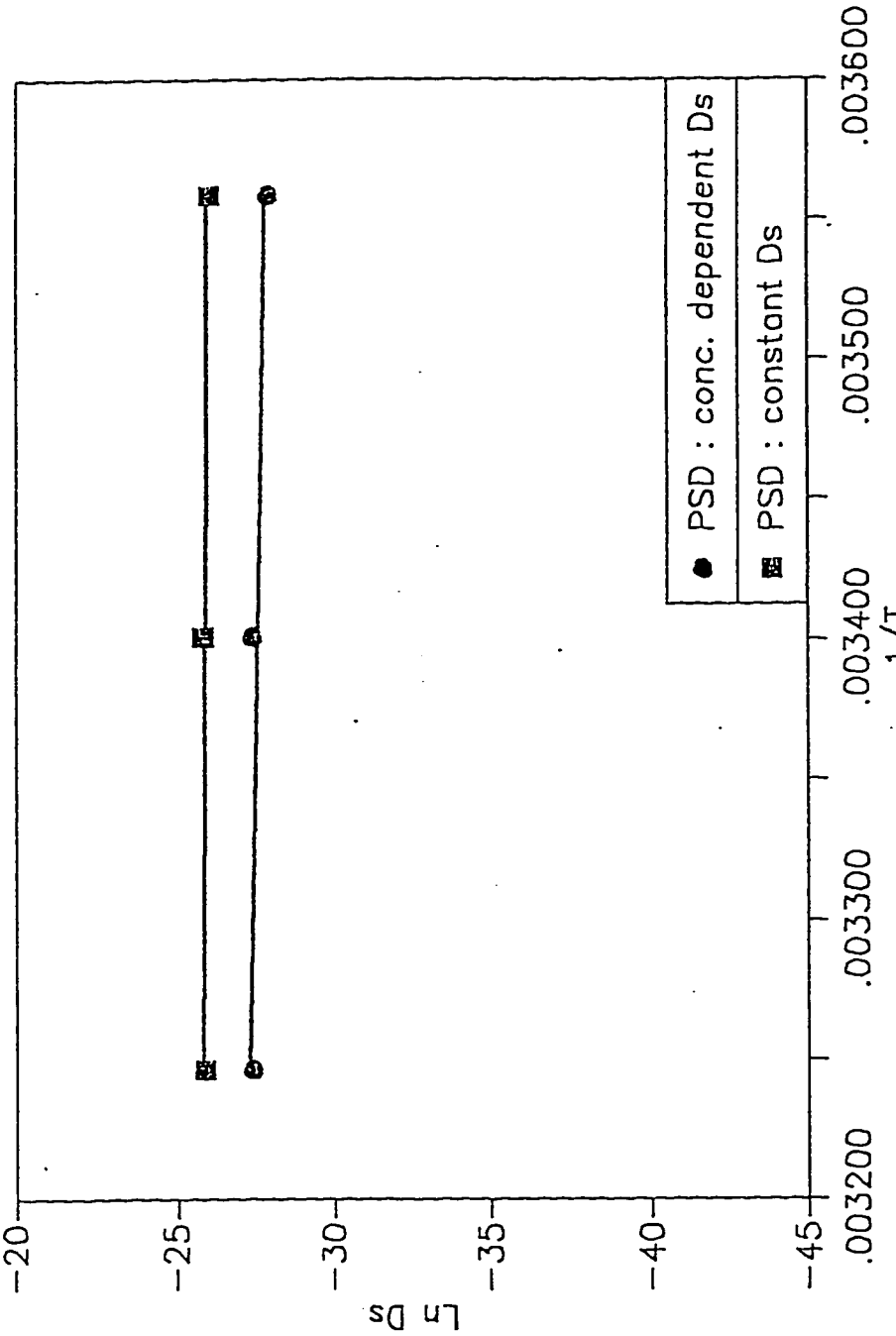


Fig 2.14: Plot of Ln Ds vs 1/T for
PSDM – Model 4 and 5. Adsorption of phenol

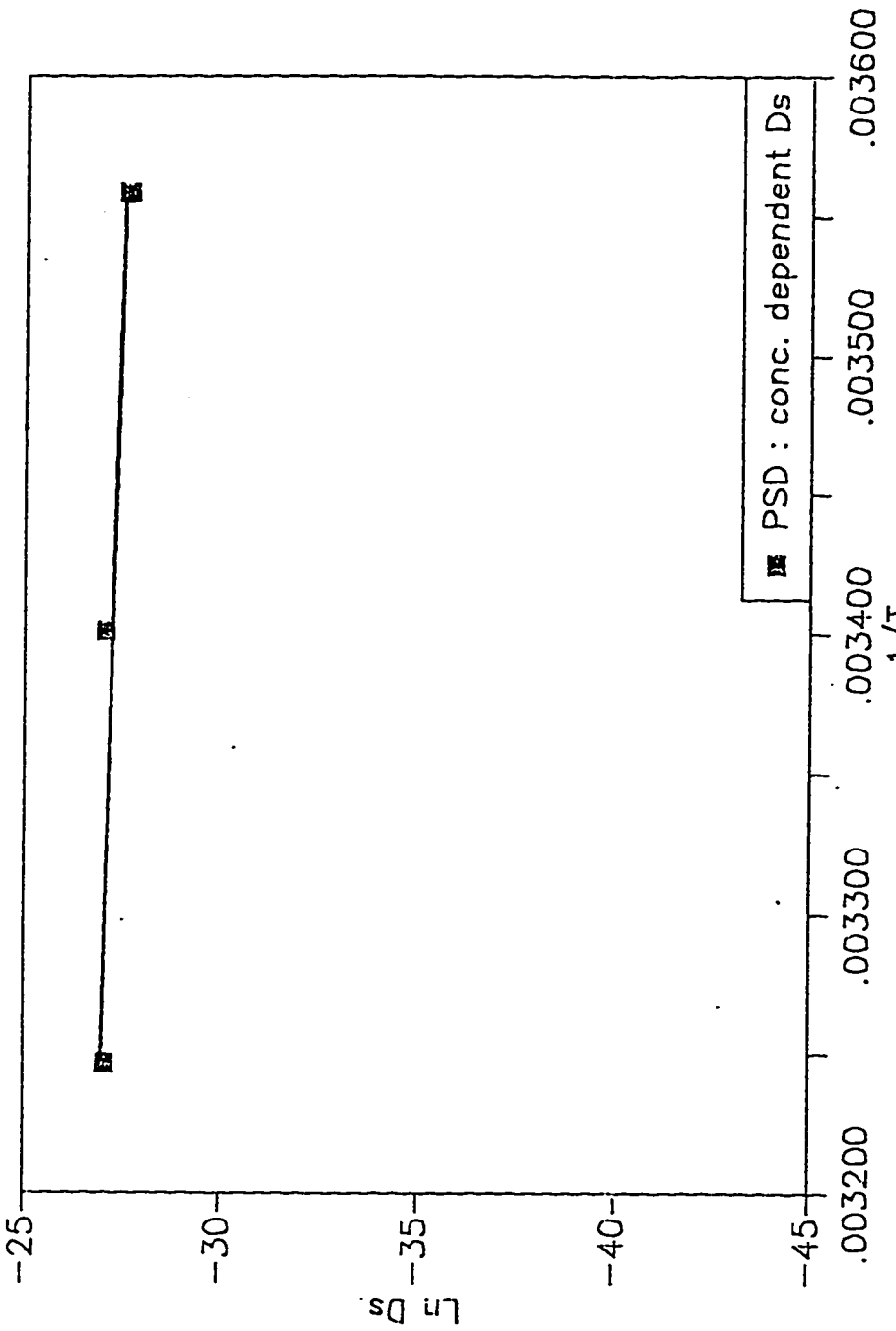


Fig 2.15: Plot of Ds vs 1/T for
HSDM – Model 3. Adsorption of o-cresol

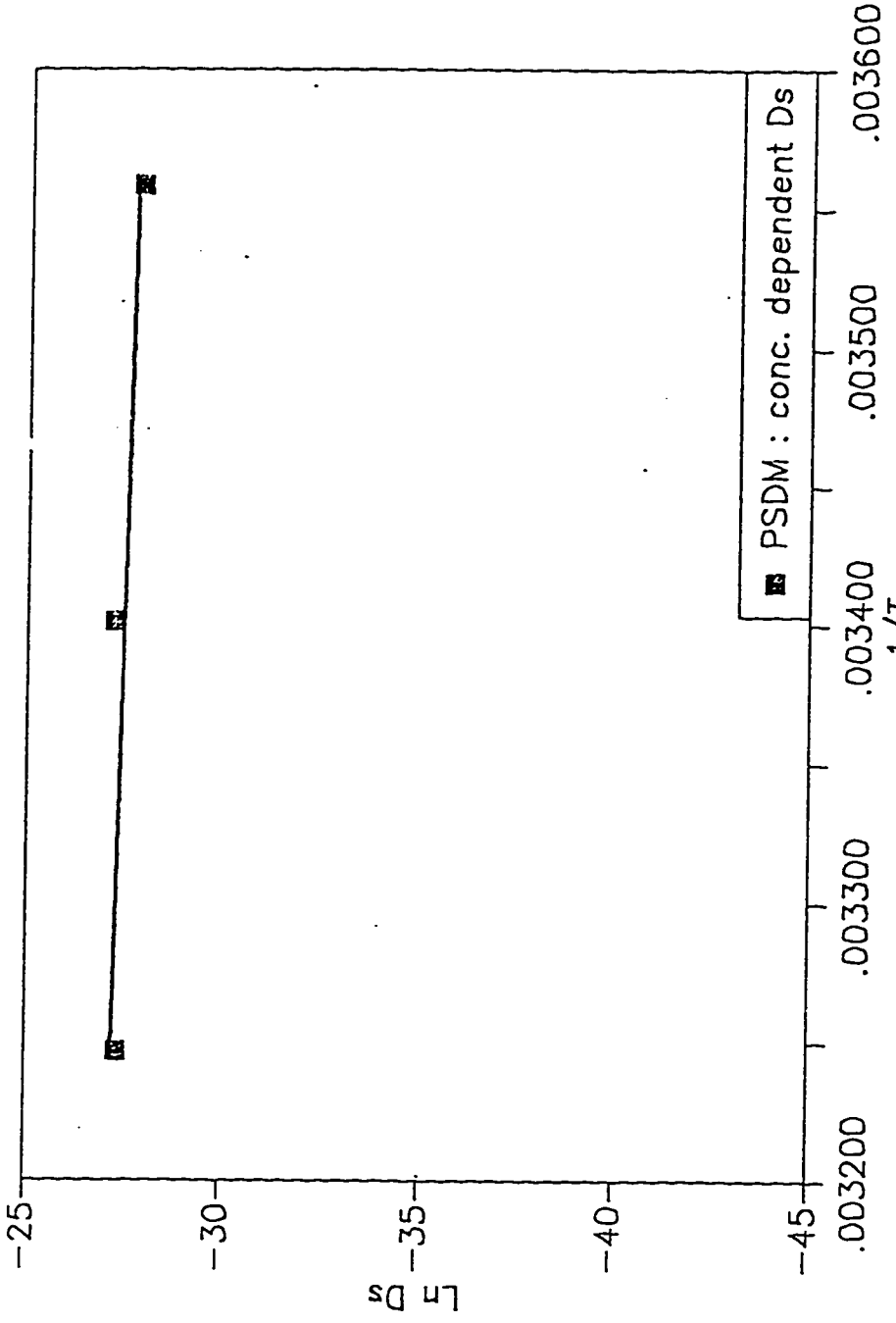


Fig. 2.16: Plot of Ln Ds vs 1/T for PSDM – model 5
Adsorption of o-cresol

$$D_{s0} = D^{*}_{s0} \exp(-E/RT) \qquad (2.66)$$

where E is the diffusional activation energy and D^{*}_{s0} is the preexponential term. The values of E and D^{*}_{s0} for phenol and o-cresol for the various models are given in Table 2.5. It may be seen from Table 2.5 that both the preexponential term and the diffusional activation energies for the constant D^{*}_{s0} are lower than those for the of the concentration dependent D_{s0} processes. This results from the fact that the surface diffusivity coefficient of the constant D_{S0} process is higher than that of the concentration dependent D_{s0} process. The surface diffusivity used for the concentration dependent process is D_{s0} which represents the diffusivity at zero adsorbent concentration or when the chemical potential gradient is the same as the concentration gradient.

The literature D_s values indicates a dependence on initial adsorbate concentration as may be seen in Table 2.4. Moreover, the value of the initial adsorbate concentration determines the suitability of the pore diffusion model in predicted the adsorption process and also affects the advantage of the PSD model over the HSDM. To access the relative contributions and importance of pore diffusion to the surface diffusion the ratio of the pore diffusion flux in equilibrium with the bulk phase concentration at the surface of the particle to that of its surface diffusion counterpart was evaluated and plotted against the bulk phase concentration. This plot is presented in Figure 2.17. The flux ratio is found to vary with temperature and the bulk phase concentration. This indicates that pore diffusion is always present and is more important at high temperatures than at low temperatures. The values of D_s as seen in Table 2.3 are approximately constant in the PSD model but vary widely with temperature in the HSDM. for both the constant and

Table 2.5 Temperature Dependence of Surface Diffusivity Coefficient

Model No.	Preexponential Term D^{*}_{s0}*E10 (m^2/.s)	Diffusional Activation Energy E (*E-4) (J/gmole)
Phenol		
2	5.1185	1.0279
3	6.4938	1.48
4	0.2558	0.364
5	1.7420	1.2330
o-cresol		
3	6.34	1.486
5	3.34	1.382

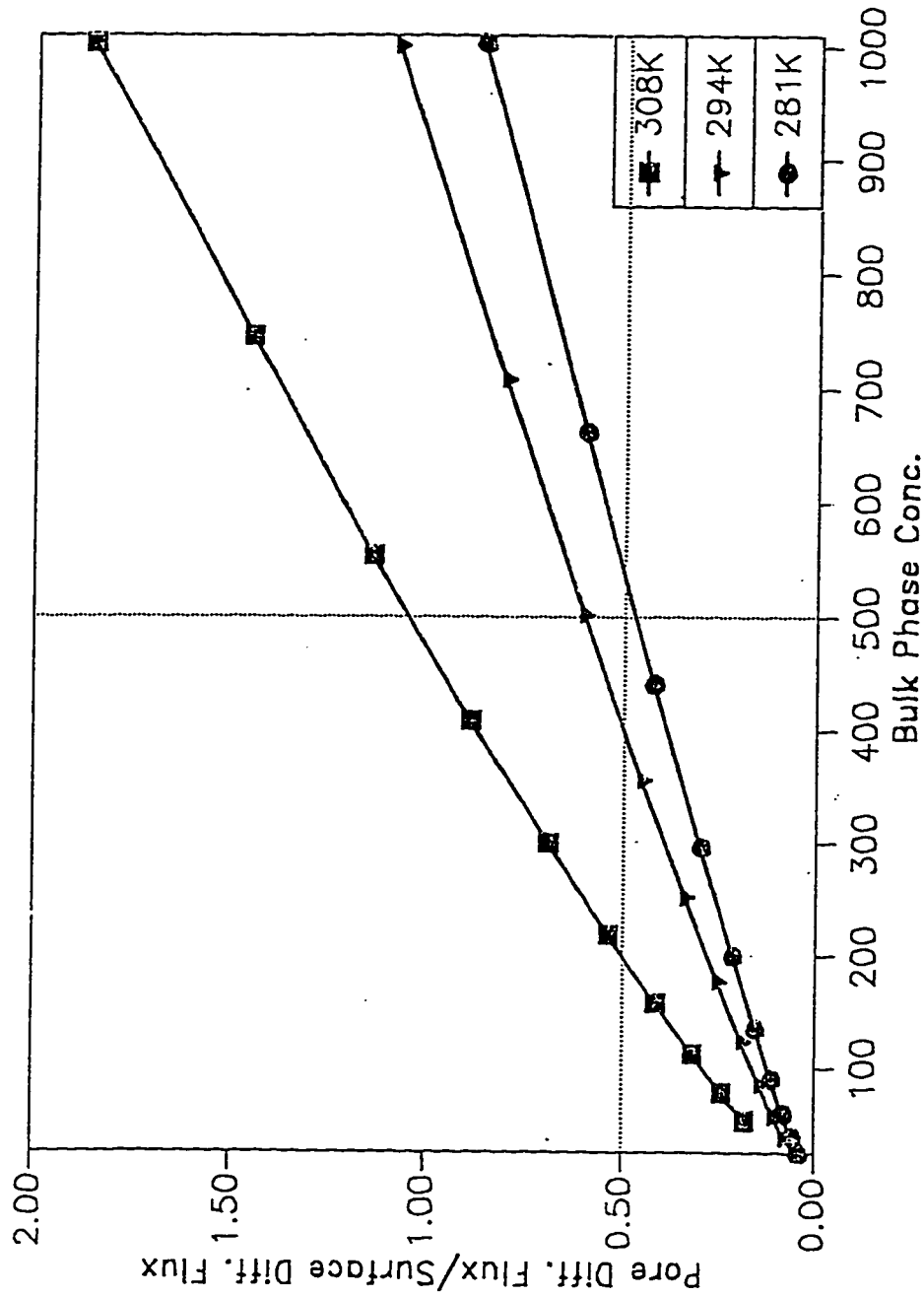


Fig.2.17: Plot of Pore Diffusion Flux/Surface Diffusion Flux Vs Bulk Phase Concentration. Adsorption of phenol

concentration dependent surface diffusivity models. The wide variation of D_s with initial adsorbate concentration that has been reported often times in literature in HSDM is due to the pore diffusion flux which increases with initial adsorbate concentration but is not accounted for.

2.5 Conclusions and Recommendations

The experimental data were fitted using five different models. These are

Model 1 : The pore diffusion model,

Model 2 : The homogeneous surface diffusion model with constant surface diffusivity coefficient,

Model 3 : The homogeneous surface diffusion model with concentration dependent surface diffusivity coefficient,

Model 4 : The pore and surface diffusion model with constant surface diffusivity coefficient, and

Model 5 : The pore and surface diffusion model with concentration dependent surface diffusivity coefficient.

Models 3 and 5, takes into account the surface energetic heterogeneity in the diffusion of adsorbed species. The Darken's relation, based theoretically on the chemical potential gradient driving force, is used to account for the dependence of surface diffusivity on solid phase concentration.

The values of the surface diffusivity coefficients were obtained by minimizing the rms. values of the normalized residuals between the experimental and predicted liquid concentrations. Relevant values are shown in Table 2.3.

The pore diffusion model gave a poor fit.

The fits of the HSDM and the PSD models with constant and concentration dependent surface diffusivity were equally good.

Recommendations

It is explicit from this study, that the PSD model is quite efficient in predicting batch adsorption process at all concentration levels. However, there is a slight degree of variation in the values of surface diffusivity coefficients with time. This needs to be accounted for by taking into consideration the surface energetic heterogeneity in the diffusion of adsorbed species. The Darken's relation, based on chemical potential gradient does not account for concentration dependence completely. This necessitates the need to investigate more fundamentally the dependence of surface diffusion coefficient on concentration and to contrive a more efficient correlation to account for it.

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2.7 Nomenclature

a	constant in Myer's isotherm.
A_i	Virial coefficients.
B	equilibrium parameter.
C_o	initial liquid phase concentration
$C_{P0}, \overline{C_p}, C_p$	initial, dimensionless, and fluid pore concentrations
C_s	concentration at surface of the particle
C_∞	fluid phase equilibrium concentration
C(t)	fluid phase concentration as function of time.
$\overline{C}(\tau)$	dimensionless fluid phase concentration as function of dimensionless time.
C_{o_2}	fluid phase concentration of oxygen as a function of time.
$C_{o_2,0}$	initial fluid phase concentration of oxygen
$C_{o_2,\infty}$	fluid phase concentration of oxygen at equilibrium
D_{eff}	effective diffusivity coefficient
$D_{e,p}$	effective pore volume diffusivity coefficient
D_p	pore volume diffusivity coefficient
D_{AB}	mutual diffusion coefficient of solute A in a dilute concentration of solvent B
D_{so}	surface diffusivity at zero adsorbate loading,

D_s	surface diffusivity coefficient
D^*_{s0}	preexponential term in surface diffusivity coefficient temperature dependence expression
k_{LF},K_i	Langmuir Freundlich isotherm constant, other isotherm constants
k	mass transfer coefficient
M_B	molecular weight of solvent B
M_t	total amount of adsorbate which diffuses from the bulk phase into the carbon particle at any time, t
M_∞	mass adsorbed at infinite time
n	Langmuir Freundlich isotherm constant
N	adsorbate flux into the particle,
q_{os}	adsorbate phase concentration in equilibrium with the initial fluid phase concentration ,
$\bar{q}_\infty$	average adsorbate concentration at infinite time
q(r, t)	adsorbent phase concentration as a function of radial position and time
$\bar{q}(t)$	average adsorbate concentration on the particle as a time, t
$\bar{Q}(\tau)$	dimensionless average adsorbate concentration as a function of dimensionless time, $\bar{q}(t)/q_{os}$
$Q(\eta,\tau)$	dimensionless adsorbent phase concentration, $q(r,t)/q_{os}$
r	radial coordinate,
r_s	particle radius,
T	absolute temperature, K
t	time

u	uptake of adsorbent ·
V_A	molal volume
V_p	total volume of the particle
W_s	mass of the carbon particle

Greek alphabet

α	solute distribution parameter(dimensionless), Wq_{os}/VC_o,
ε_p	porosity of the particles
ρ_p	density of particle
η	dimensionless radius
η_B	viscosity of solvent B, cp
θ	loading, $\frac{q}{q_s}$
λ	loading, $\frac{q_o}{q_s}$
τ	dimensionless time
τ_p	tortuosity factor.

CHAPTER THREE

DIFFUSION AND REACTION IN BATCH SYSTEMS

3.1 Introduction

Activated carbons are known to have surface oxides groups (or oxygen complexes). These can arise from chemical adsorption of air or pure oxygen (oxidation) during the activation stage or during storage after activation. Also, the surface oxides can be produced by oxidation of carbon samples with aqueous solutions of oxidizing agents (Studebaker et al., 1956; Garten et al., 1957).

The oxide groups present on the surface of the GAC alters its adsorption characteristics and capacity. These oxides groups are directly responsible for the oxidative coupling reactions that occur on the surface of the GAC and are presumably catalyzed by it. The concentration of these oxides or else the degree of oxidation of the GAC is a determining factor of the magnitude of the reaction rate. The degree of oxidation, of course is directly related to the concentration of oxygen or oxidizing agent employed in the activation stage.

3.2 Literature Survey

The oxygen chemisorbed on carbon exists mainly in the form of four different acidic surface groups. These are :

(i) strong carboxylic groups,

(ii) weak carboxylic groups which exist as lactone groups

combined with the neighboring carbonyl groups,

(iii) phenolic groups ,

(iv) carbonyl groups which form lactone groups with carboxyl groups of type (ii) (Boehim et al., 1964).

Surface oxide groups can be removed by heat treatment of carbons in an inert atmosphere or under vacuum. The sorption characteristics and capacity of activated carbon is influenced by the surface functionality. Two different approaches have been followed in evaluating the influence of these surface oxide groups. The direction and magnitude of this influence with respect to the adsorption of phenol is directly dependent on the approach adopted. Past researchers oxidized the carbon prior to the adsorption process using various oxiding agents, whereas recent researchers conducted the adsorption and oxidation processes simultaneously.

Coughlin (1970) reported that the oxidation of activated carbon by potassium permanganate solution increases the acidic oxides concentration on the surface. This lowered both the capacity and the rate of sorption of phenol. Snoeyink et al. (1974) found that oxidation with aqueous chlorine increased the acidic oxides concentration on activated carbon. This resulted in a decrease in sorption capacity for phenol and nitrophenol by about 50%. Subsequent to these findings, Prober et al. (1975) reported that sorption of nonpolar species should be impaired as a result of increasing surface oxides. Prober et al. further asserted that since carbon sorption of oxygen invariably increases the surface acidic oxides, a decrease in the sorption capacity for phenol is inevitable. However, his investigation showed that this decrease is

negligible in view of the small oxygen demand which would be exerted by activated carbon at normal dosages for wastewater treatment. Magne and Walker (1986), showed that chemisorption of oxygen on activated carbon at 573K prior to phenol adsorption reduces the initial capacity of the carbon for the retention of phenol.

Recent researchers urshered in an incisively different approach. The findings of previous researchers are diametrically opposed to that of the present ones. The formation of the surface oxides due to oxidation with dissolved oxygen is seen to have auspicious effects on phenolic adsorption by GAC. Vidic et al., (1990), investigated the influence of molecular oxygen on the adsorptive capacity of GAC. Their results showed a considerable increase in the GAC adsorptive capacity for various compounds under aerobic conditions. The adsorptive uptake of GAC under aerobic conditions increases for o-cresol by 22- 200% over that attainable under anaerobic conditions. The same trend was observed for 3- ethylphenol (18-92% increase) and phenol (42-85% increase). This increase was attributed to the chemical reaction between the adsorbed phenol and the oxygen adsorbed on the surface of the carbon. This reaction was presumably catalyzed by the carbon surface. The reaction occurs on a different (slower) time scale from physical adsorption. Similar results were reported by Vidic and Suidan (1992).

The work of Grant and King (1990) also showed that dissolved oxygen increases the adsorptive capacity of GAC. Their experiments showed that oxidative coupling of phenolic compounds on carbon surfaces was plausibly responsible for irreversible adsorption. The irreversible adsorption

on the carbon surface has been attributed to chemical reaction of sorbate molecules with oxygenated surface functional groups (Mattson et al.,1969; Modell et al.,1980; Puri , 1980; Chang et al., 1981; Yonge et al.,1985). This was supported by Grant and King (1990). Furthermore, Grant and King discovered that the presence of oxygen increases the total and irreversible adsorptive uptake of phenol by GAC. Their results showed that the chemical reaction is very slow compared to physisorption, and hence was rate limiting.

Cooney and Xi (1992) examined the kinetics of activated carbon catalyzed oxidative coupling reactions of phenolic compounds. They observed that after the initial rapid adsorption process had occurred, there was a slow but steady decline in solution concentration over a period of many days and weeks. They attributed these slow changes to oxidative coupling reactions. These reactions occurring on the carbon surface produces strongly adsorbed polymeric products. The coupling reactions reduces the phenol concentration creating free sites for phenol to be transferred from the solution. They concluded that although oxidative coupling reactions can occur in the absence of dissolved oxygen, its presence markedly accelerated them.

Abuzaid and Nakhla (1994) studied the effect of dissolved oxygen on activated carbon uptake. The influence of different dissolved oxygen levels at various temperatures and pHs were examined. Their results supported those of Vidic et al., Grant and King; and Cooney and Xi. The dissolved oxygen level definitely increases the adsorptive capacity of GAC. The uptake for phenol, o-cresol, and nitrophenol at 1mg/l under aerobic

conditions were respectively 163%, 114%, and 18% higher than the anaerobic uptakes. The increase in the GAC uptake was in direct proportion to the dissolved oxygen level. At constant temperature and pressure for a given adsorbate-adsorbent system, the increase in adsorption capacity was solely dependent on the mass of GAC and mass of dissolved oxygen. The increase in GAC uptake was shown to be the result of oxidative coupling reactions primarily occurring on the surface of the carbon. The reactions which ares catalyzed by the carbon surface takes place plausibly between the physisorbed sorbate and chemisorbed oxygen molecules. The products of the oxidative coupling reactions were identified as 2,2-dihydroxy-1, 1-biphenyl, 4-phenoxyphenol and a phenolic trimer.

Vidic and Suidan (1994) studied the impact of oxygen mediated oxidative coupling on adsorption kinetics of 2-methylphenol. They observed that for the initial phase of 12 hr., the aqueous phase concentration of the 2-methylphenol in anoxic bath rapidly reach equilibrium level, while it took almost 12 days in the oxic bath. It was noted that for the first 12 hr., the time dependent concentration profile of both the oxic and anoxic baths were indistinguishable. The adsorption capacity was clearly higher for the oxic case. Their attempt to evaluate the effect of GAC particle size on adsorption capacity was reportedly fruitless.

Grant and King (1990) found that the carbon surface catalyzed oxidative coupling reactions increases with temperature. Hence higher temperatures corresponds to higher GAC adsorption capacity. Also, the coupling reactions were promoted by high pH. and temperature.

Cooney and Xi (1992) studied the effect of pH on the adsorptive capacity of GAC in the presence of dissolved oxygen. They showed that at pH 2 and pH 7, the initial amount adsorbed was the same. At these pH values, phenol with a pka value of 9.99 was essentially 100% undissociated. At pH 12, however, the phenol totally dissociated. It is a known fact that ionized forms of species adsorbs far less on activated carbon than do their undissociated forms. Thus, the initial amount of adsorbed phenol was less at pH 12 than at pH 7. However, the oxidative coupling reactions were reportedly promoted by high pH. At pH 2 the reactions were minimal. The reaction rate at pH 12 was faster than at pH 7. The pH of the solution and not the degree of dissociation is the important determinant of the reaction.

Abuzaid (1993) contended that the net effect of the pH and temperature on activated carbon adsorption is a combination of their influence on both physical adsorption and the coupling reactions. Physical adsorption was favored at 3, while the highest sorbate uptake occurred at pH 11. He quoted pH 7 as the optimum value for adsorption of phenolics by activated carbon under aerobic conditions. He observed that anaerobic adsorption of phenol and o-cresol increased with decreasing temperature and was highest at the lowest temperature studied (8C). The promotion of adsorption by the oxidative coupling reactions was greatest at 35C. The aerobic isotherms showed little dependence on temperature. This suggests that the positive and adverse influence of temperature on chemical reactions and physical adsorption respectively annuls each other.

3.3 Theoretical Model

The pore and surface diffusion model with concentration dependent surface diffusivity coefficient was used. The general assumptions made in formulating the model have been presented in chapter two of this work. The Darken's relation was used to account for the concentration dependence of diffusivity. This model can easily be converted to the homogenous surface diffusion model by setting the pore diffusion coefficient to zero.

The Darken's relation yields the following expression for the surface diffusivity coefficient.

$$D_s = D_{so} \frac{d \ln C_P}{d \ln q} \qquad 3.1$$

The three possible ways of defining the reaction term, R are :

(I) zero order in adsorbate, and proportional to the oxygen imbalance,

(ii) first order in adsorbate, and proportional to the oxygen imbalance,

(iii) m th order in adsorbate, and proportional to the oxygen imbalance to the n' order.

The general pore and surface diffusion model with reaction term added becomes :

$$\left[\frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q}+1\right]\frac{\partial q}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left\{r^2\left[D_p\frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q}+D_{so}\frac{d\ln C_P}{d\ln q}\right]\frac{\partial q}{\partial r}\right\}-R \qquad 3.2$$

$$\text{As } \frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q} << $$

this term may be neglected since it is much less than one. The adsoprtion - reaction equation reduces to

$$\frac{\partial q}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left\{r^2\left[D_p\frac{\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q} + D_{so}\frac{d\ln C_p}{d\ln q}\right]\frac{\partial q}{\partial r}\right\} - R \qquad 3.3$$

where the first term on the right hand side is the pore diffusion term, the second term is the concentration dependent surface diffusivity term, and the third term , R is the reaction term. The reaction term R is defined as :

$$R = k_{o_2} k_{phe} q^m \left(q_{o_2} - q_{o_2,\infty}\right)^{n'} \qquad 3.4$$

where m and n' can take any value depending on the best fit of the experimental data.

Therefore the general adsorption - reaction equation becomes :

$$\frac{\partial q}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left\{r^2\left[\frac{D_p\varepsilon}{\rho_p}\frac{\partial C_p}{\partial q} + D_{so}\frac{d\ln C_p}{d\ln q}\right]\frac{\partial q}{\partial r}\right\} - k_{o2} k_{phe} q^m \left(q_{o2} - q_{o2,\infty}\right)^{n'} \qquad 3.5$$

The initial conditions are clean adsorbent and the boundary conditions are those for a finite bath subject to nonlinear Langmuir - Freundlich adsorption .

Langmuir -Freundlich adsorption isotherm.

The Langmuir - Freundlich adsorption isotherm is :

$$\frac{q}{q_s}=\frac{k_{LF}C^{1/n}}{1+k_{LF}C^{1/n}} \qquad 3.6$$

Defining the following dimensionless groups:

$$\tau=\frac{D_{so}t}{r_s^2};\eta=\frac{r}{r_s};Q=\frac{q}{q_{os}};\lambda=\frac{q_{os}}{q}=\frac{k_{LF}C_o^{1/n}}{1+k_{LF}C_o^{1/n}};X=\frac{\varepsilon n D_p}{\rho_p k_{LF}^n q_s D_{so}};$$

$$K=\Phi^2\left(\frac{r_s^2}{D_{so}}\right)^{-n''}\left(C_{o_2,o}-C_{o_2,\infty}\right)q_{os}^{m-1}Hk';\Phi=\sqrt{\frac{r_s^2k_{o_2}k_{phe}}{D_{so}}}$$

The surface diffusivity and isotherm gradient in dimensionless form based on the Langmuir-Freundlich adsorption isotherm become:

$$D_s=D_{so}\frac{d\ln C_p}{d\ln q}=D_{so}\frac{n}{(1-Q\lambda)};\frac{\partial C_p}{\partial q}=\frac{n}{k_{LF}^n q_s}\frac{(Q\lambda)^{n-1}}{(1-Q\lambda)^{n+1}} \qquad 3.7$$

Assuming the bulk phase concentration of oxygen is linearly related to the adsorbed phase concentration, we have

$$q_{o_2}=HC_{o_2} \qquad 3.8$$

Then :

$$\frac{q_{o2}-q_{o2,\infty}}{q_{o2,0}-q_{o2,\infty}}=\frac{C_{o2}-C_{o2,\infty}}{C_{o2,0}-C_{o2,\infty}} \qquad 3.9$$

The data of Suidan and Vidic for oxygen in the reactor when plotted logarithmically versus time gave a straight line having the following relationship.

$$\frac{q_{o_2}-q_{o_2,\infty}}{q_{o_2,0}-q_{o_2,\infty}}=\frac{C_{o_2}-C_{o_2,\infty}}{C_{o_2,0}-C_{o_2,\infty}}=k't^{-n''} \qquad 3.10$$

where -n" is the slope of the log - log plot of $\frac{C_{o2}-C_{o2,\infty}}{C_{o2,0}-C_{o2,\infty}}$ versus time and the natural logarithm of k'is the abscissa intercept. Therefore we conclude that

$$q_{o_2}-q_{o_2,\infty}=H\left(C_{o_2,0}-C_{o_2,\infty}\right)k't^{-n''} \qquad 3.11$$

and R becomes

$$R=\left(\frac{r_s^2}{D_{so}}\right)k_{o_2}k_{phe}q_{os}^{\,m-1}Q^m\left[H\left(C_{o_2,0}-C_{o_2,\infty}\right)k'\left(\frac{r_s^2}{D_{so}}\right)^{-n''}\tau^{-n''}\right]^{n'} \qquad 3.12$$

In this work, the value of n' was assumed to be one. The reaction term can be rearranged into the following :

$$R=\left(\frac{r_s^2}{D_{so}}\right)\left(\frac{r_s^2}{D_{so}}\right)^{-n''}\left(C_{o_2,0}-C_{o_2,\infty}\right)k_{o_2}k_{phe}q_{os}^{\,m-1}Q^mHk'\tau^{-n''} \qquad 3.13$$

In dimensionless form the reaction term becomes :

$$R=\left(\frac{r_s^2}{D_{so}}\right)\left(\frac{r_s^2}{D_{so}}\right)^{-n''}\left(C_{o_2,0}-C_{o_2,\infty}\right)q_{os}^{\,m-1}Q^mk'k_{o_2}k_{phe}H\tau^{-n''} \qquad 3.14$$

The reaction term simplifies to :

$$R=KQ^m\tau^{-n''} \qquad 3.15$$

where K is the combined parameter.

The final adsorption - reaction equation becomes:

$$\frac{\partial Q}{\partial \eta} = \frac{1}{\eta}\frac{\partial}{\partial \eta}\left\{\eta^2\left[X\frac{(Q\lambda)^{n-1}}{(1-Q\lambda)^{n+1}} + \frac{n}{(1-Q\lambda)}\right]\frac{\partial Q}{\partial \eta}\right\} - KQ^m\tau^{-n''} \quad 3.16$$

In this work, the value of n is assumed first order due to lack of data to establish the order. The final adsorption -reaction equation (eqn 3.16) was solved for the initial and boundary conditions mentioned above using the Crank-Nicolson finite difference method.

3.4 Results and Discussion

The methodology of the modeling is as follows :

(i) The order of the reaction with respect to the adsorbed adsorbate, m (o-cresol and phenol) concentration was assumed. Specific values of m assumed are 0, 1, 2, and 3; but only 1 and 2 gave reasonable fits.

(ii) The IMSL optimization subroutine, BCPOL was used to obtain the best pair of values of n", the slope of the log-log plot of the oxygen imbalance and time; and K, the overall rate constant by minimizing the root mean square (RMS) of the residuals between predicted and experimental concentration values.

(iii) The IMSL optimization subroutine, BCPOL was used to obtain the best sets of values of m, n" and K . No assumptions was made in this case..

Step (iii) gave the best value of n" to be 0.6 and the best adsorbate concentration order to be first. Step (ii) also gave the value of n" to be 0.6 with a variance with temperature. A fixed value of n" = 0.6 was used for the

three different temperatures as this is consistent with the fixed initial oxygen concentration of 8mg / L which was used for all the runs.

The optimization results for K, n" and RMS at the three different temperatures are presented in Table 3.1 and the fit of the model to the data is presented in Figures 3.1 to 3.6. Inspection of the root mean square (RMS) values in Table 3.1 reveals that the reaction order for the adsorbate favors first order. However, the differences in RMS values of the first order and second order plots are quite small. Consequently, an additional basis of judgment is needed to truly certify the order of the reaction.

The overall reaction rate constant, K increases with temperature as expected in the case of o-cresol. However, in the case of phenol, the value of K increases for the first two temperatures, (281K and 294K) but dropped at the last temperature (308K). A close scrutiny of the data at 308K, reveals a trend that is not quite the same as the trend observed in the data at 281K and 294K. The anomaly experienced at 308K could be attributed to errors in experimental readings. This point is excluded from the regression.

A plot of the natural logarithm of K versus inverse of temperature gives a straight line and is presented in Figure 3.7. The rate constant varies with temperature as follows:

$$K=K_o \exp\left(\frac{-E_a}{RT}\right) \qquad 3.17$$

Values of K_o and E_o are included in Table 3.1. The activation energies are a complex sum of rate, adsorption and diffusion activation energies and range from 322 to 1123 cals/mole.

Table 3.1:Reaction orders and overall constants for batch systems.

Temp	order = 1		order = 2	
K	n" = 0.60		n" = 0.60	
	K*E-3	RMS	K*E-3	RMS
Phenol				
281	32.0	.1336	57.0	.1424
294	36.0	.1662	58.0	.1974
308	38.0	.1686	60.0	.1803
	$K_o * E-2 = 1.89$		$K_o * E-2 = 81.4$	
	$E_a = 755$(cal / mole)		$E_a = 1123$(cal / mole)	
o-cresol				
281	48.0	.2904	106.	.3160
294	51.0	.2529	116.	.2789
308	48.0	.2730	90.	.2882
	$K_o * E-2 = 2.30$		$K_o * E-2 = 1..02$	
	$E_a = 1080$(cal / mole)		$E_a = 322$(cal / mole)	

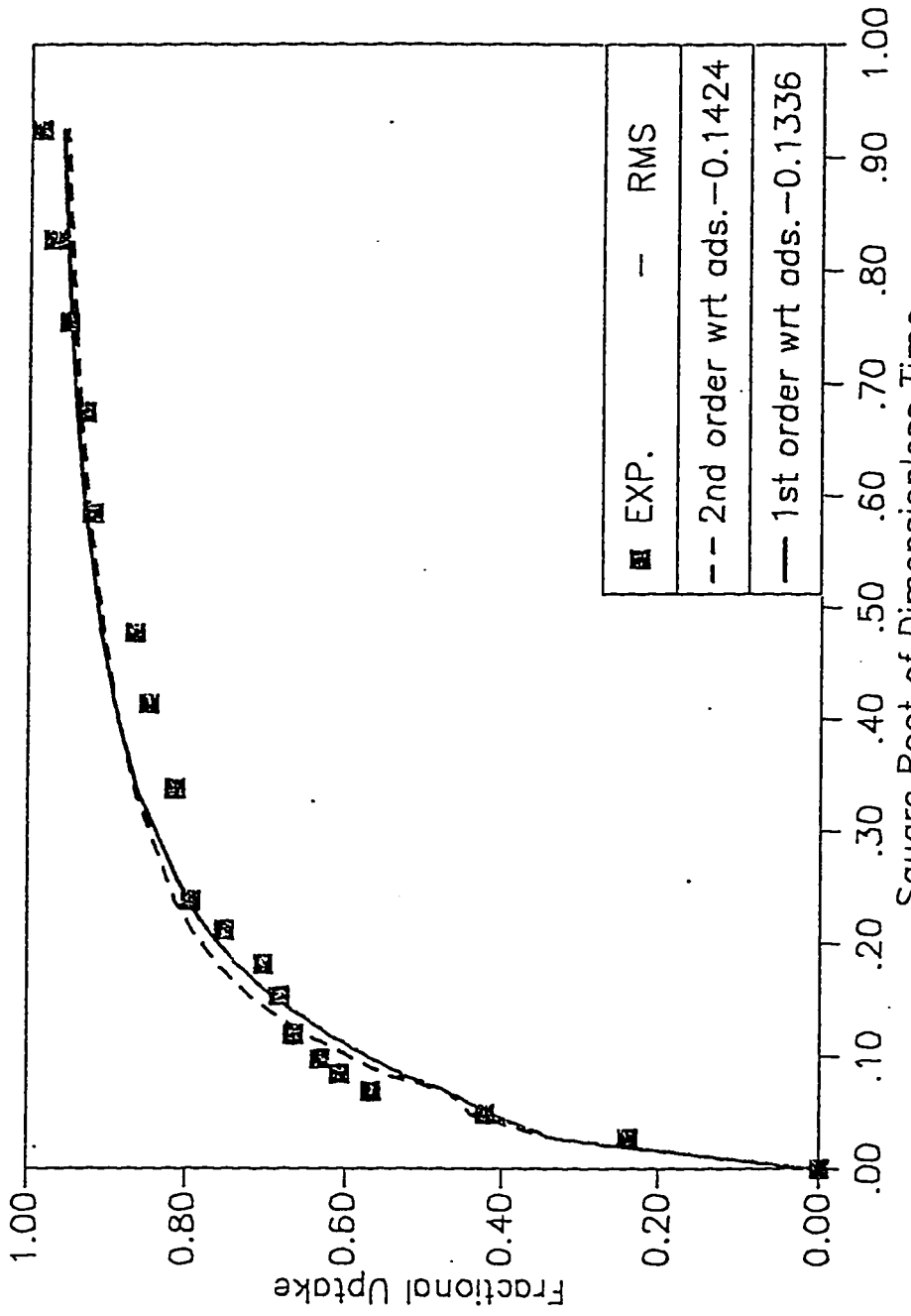

Fig 3.1: Predicted and Experimental Fractional Uptake at 281K. Adsorption with reaction of O—Cresol.

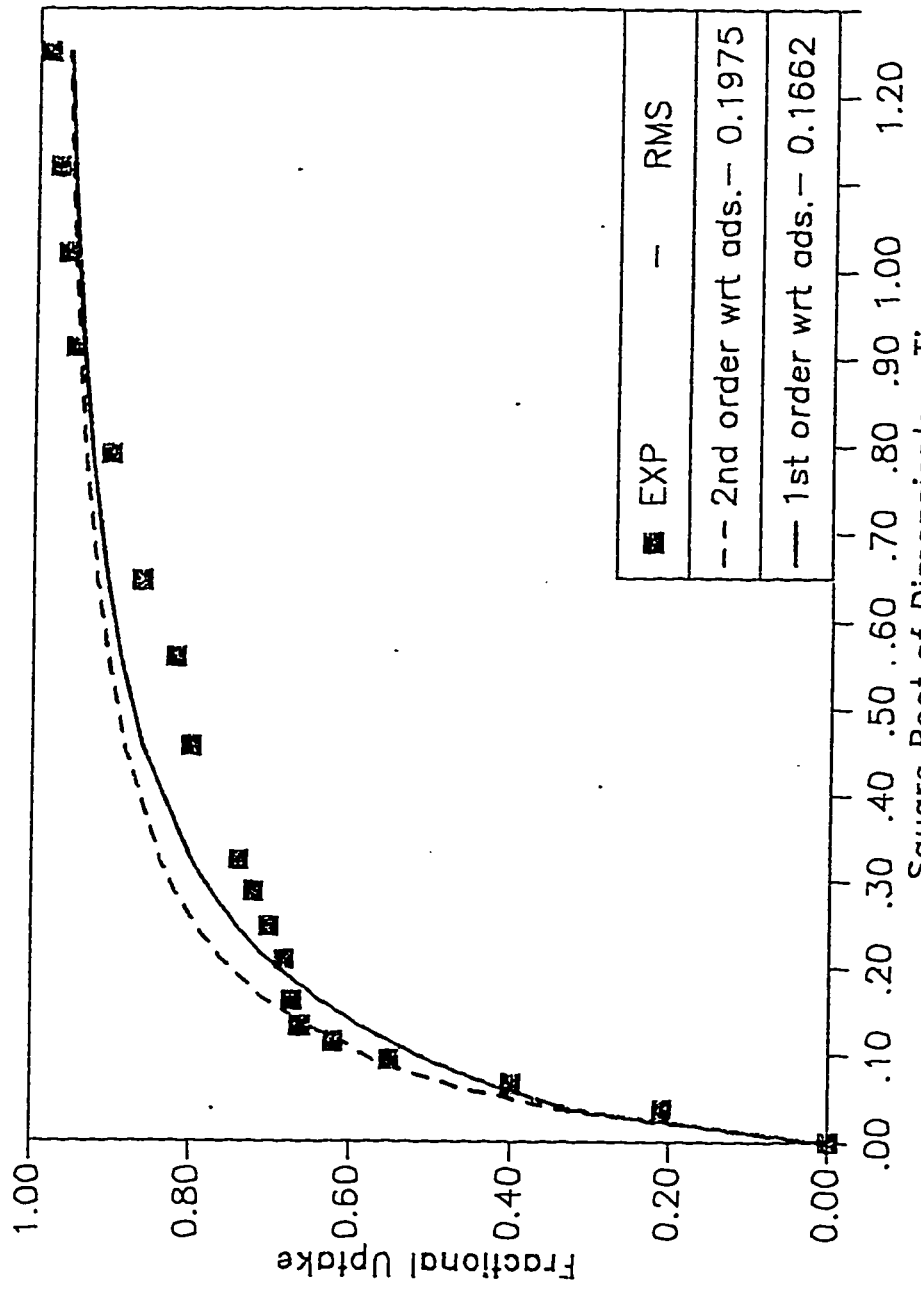

Fig 3.2: Predicted and Experimental Fractional Uptake at 294K. Adsorption with reaction of o-cresol

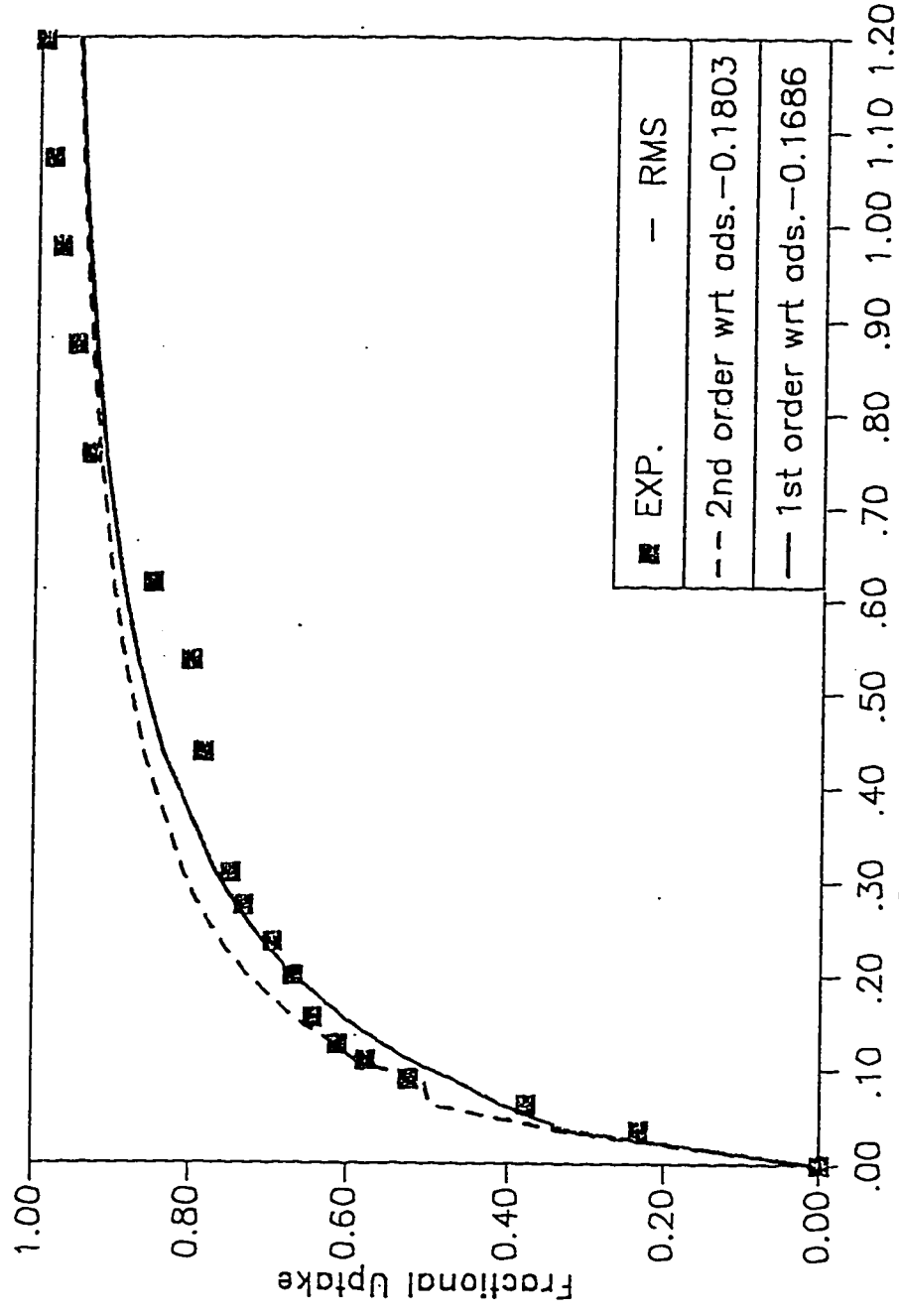

Fig 3.3: Predicted and Experimental Fractional Uptake at 308K. Adsorption with reaction of o-cresol

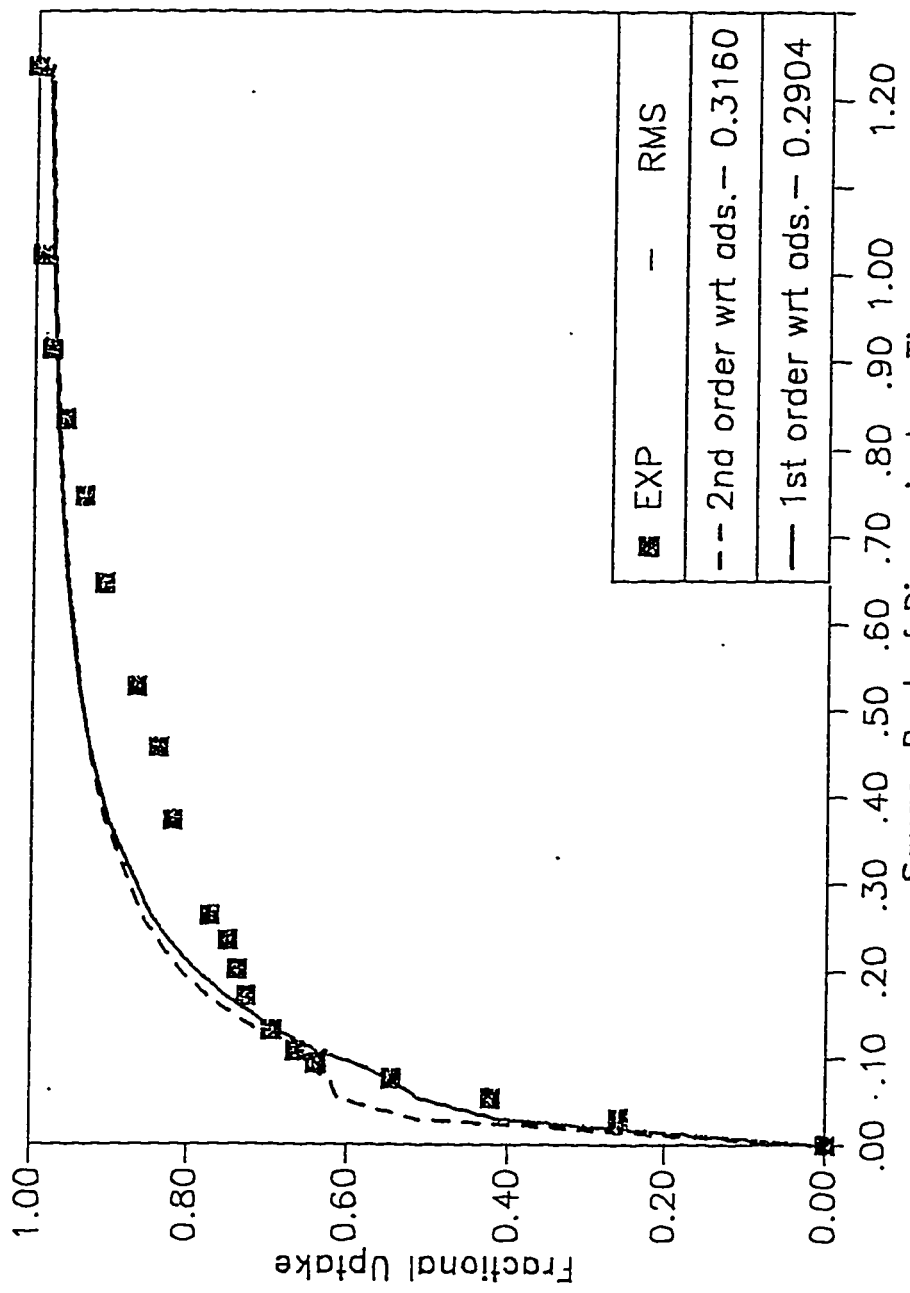

Fig 3.4: Predicted and Experimental Fractional Uptake at 281K. Adsorption with reaction of Phenol.

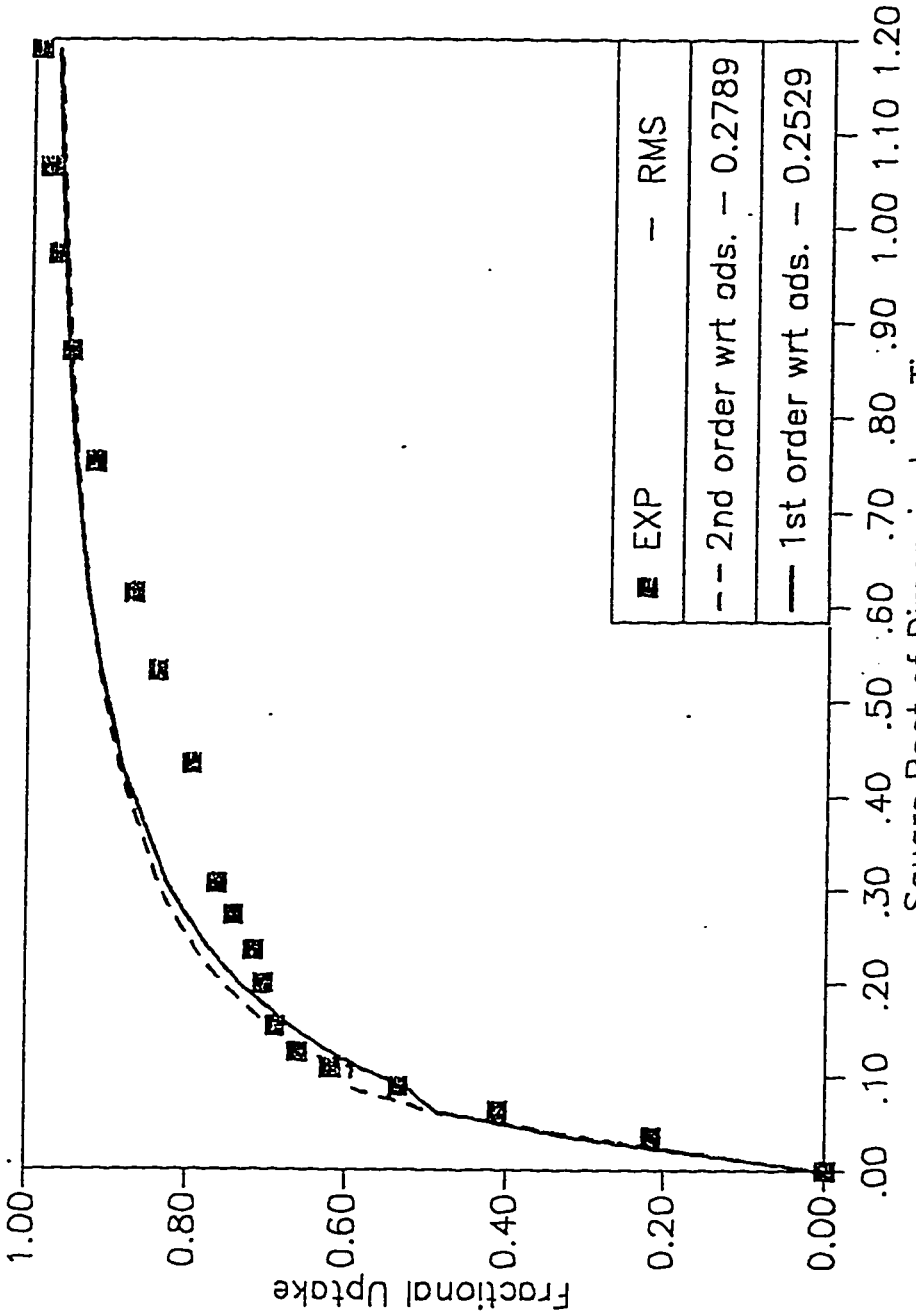

Fig 3.5: Predicted and Experimental Fractional Uptake at 294K. Adsorption with reaction of Phenol.

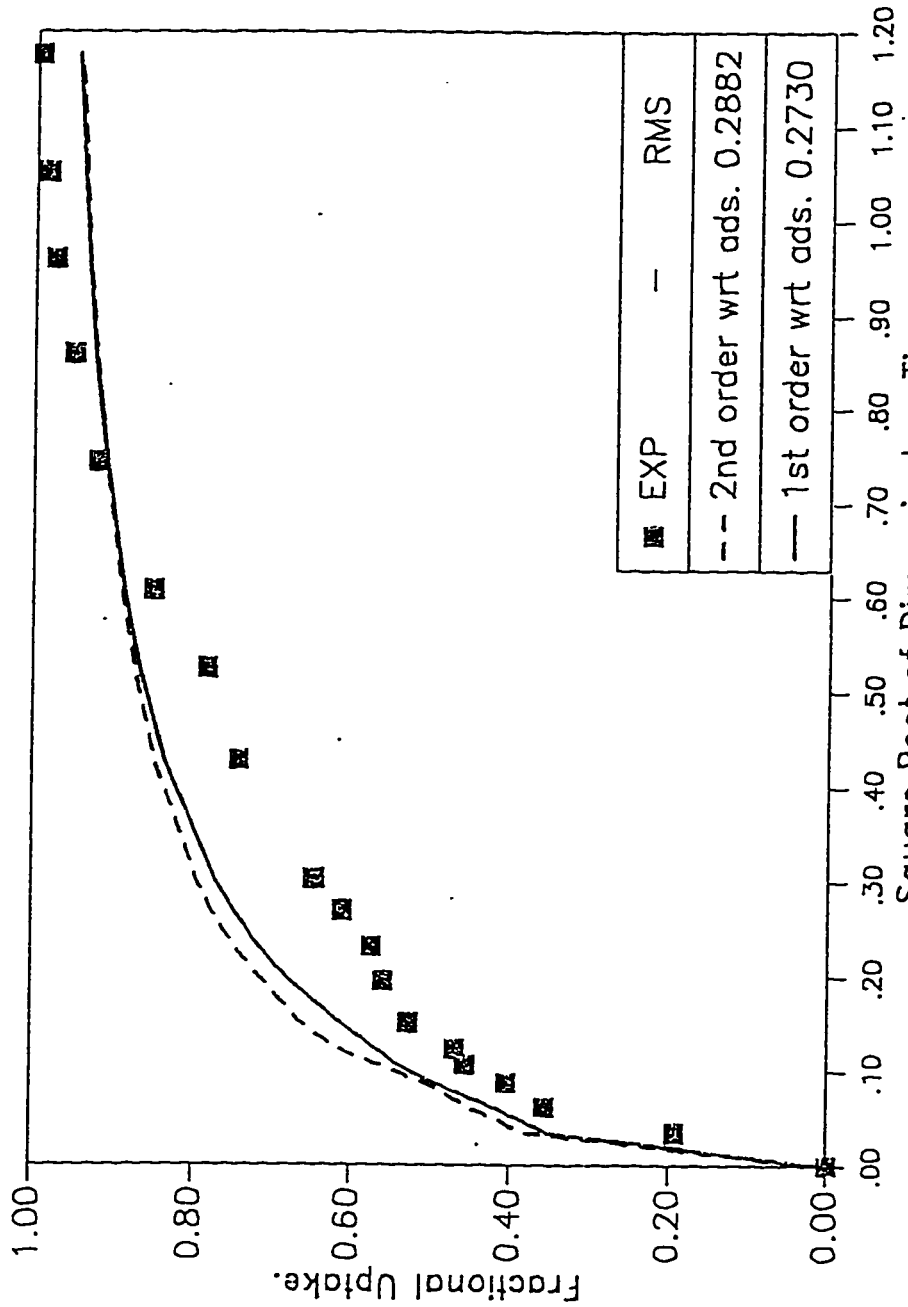

Fig 3.6: Predicted and Experimental Fractional Uptake at 308K. Adsorption of phenol with reaction

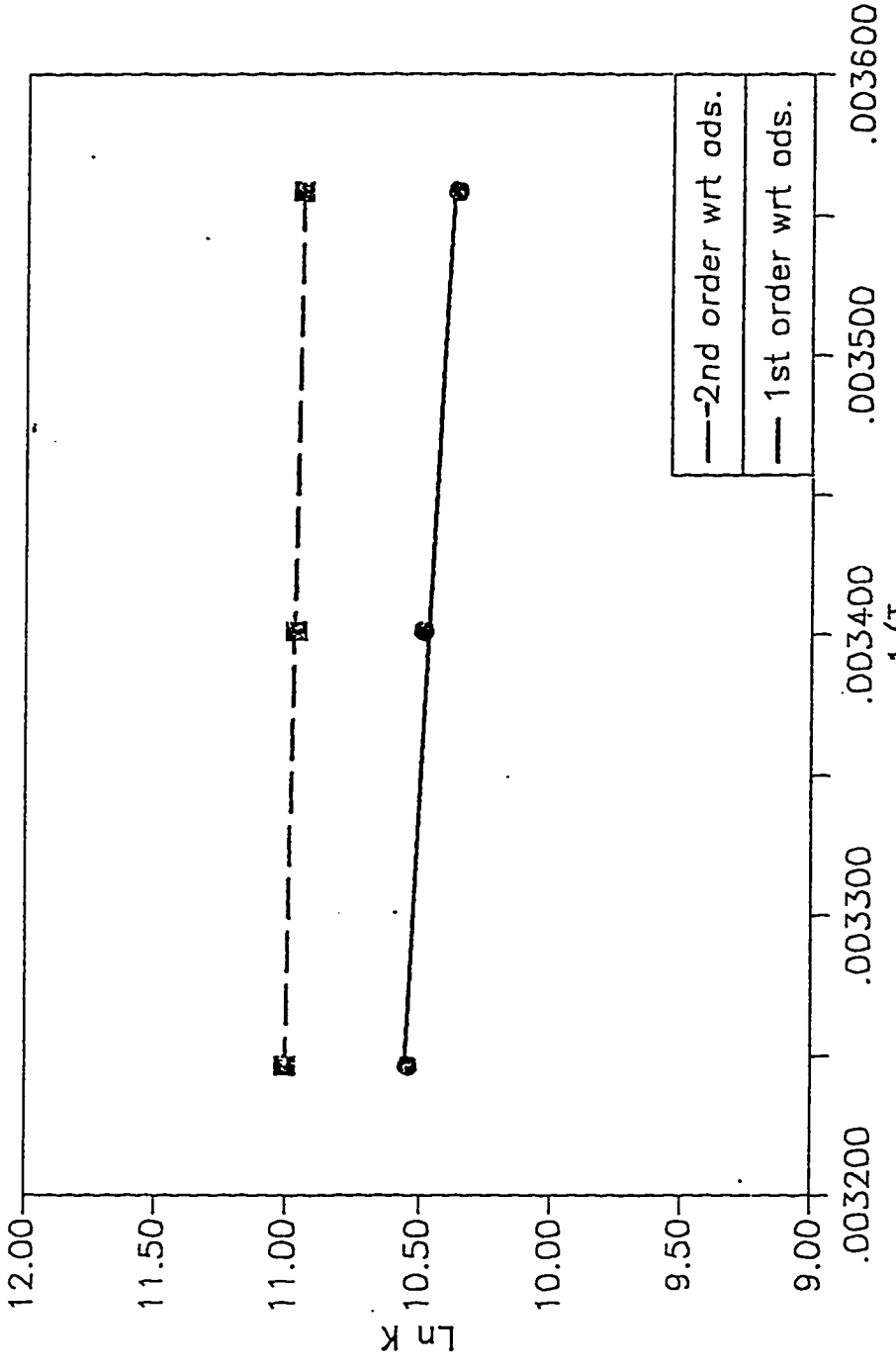

Fig 3.7: Plot of Ln K vs 1/T
Adsorption with Reaction of o-cresol

The simple empirical form of the reaction rate expression is

$$R = K \frac{Q^m}{\tau^{n''}} \qquad 3.18$$

that is, the reaction rate is proportional to sorbate concentration and inversely proportional to the time of the reaction. It is worth pointing out that the inverse proportionality to time resulted from the oxygen adsorption rate. As reaction progresses, two factors act in opposite directions. Hence, a maximum rate will occur somewhere during the reaction.

On the basis of the understanding gained from this work, the following reaction mechanism may be proposed. The sorbate molecules diffuses to the surface of the GAC and are adsorbed. Similarly, the oxygen molecules diffuses to the surface of the GAC particles and are adsorbed. Reaction of the sorbate molecules and the oxygen molecules occur on the surface of the GAC and are catalyzed by it. (Grant and King, 1990; Abuzaid, 1993).

If the reaction order with respect to the sorbate concentration is assumed to be first, then dissociation of the oxygen molecules occurs before reaction with the sorbate molecules. On the contrary, if the order is second, then the adsorbed oxygen molecules react directly with the sorbate molecules. The adsorption sites are thus occupied by sorbate and oxygen molecules that reacts creating new empty sites. The empty sites allow room for more adsorption. As time progresses, the site gets more occupied, and the reaction and adsorption decrease. From the nature of the reaction products extracted from the GAC (Abuzaid, 1993), we expect some complex interactions among the adsorbed and/or in coming molecules on the surface of the GAC.

3.5 Conclusions and Recommendations

The study presents a simple empirical rate form for predicting the reaction rate of adsorption with reaction of o-cresol and phenol in aqueous media. The reaction rate form was assumed to be m th order in adsorbate, and proportional to the oxygen imbalance to the n order.

The reaction order with respect to oxygen imbalance, n' was assumed to be first. The reaction order with respect to adsorbate concentration, m favor first order. However, the differences in RMS values of the first and second order plots are quite small. The overall rate constants increases with temperature as expected not withstanding the anomaly that was experienced at 308K in case of Phenol. The activation energies are a complex sum of

rate, adsorption and diffusion activation energies and range from 322 to 1123cals/mole.

This work is not in anyway complete in itself to truly certify the reaction order with respect to adsorbate concentration and the actual mechanism involved in the reaction. Further experimental work is needed in conjunction with this work to ascertain the actual reaction orders and mechanism. Also, it is recommended that a mass transfer equation be written for the diffusion of oxygen and solved in conjunction with that for phenol. This will eliminate the requirement for specifying the reaction rate with a time dependence.

3.8 Literature Survey

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3.9 Nomenclature

C_o initial phase concentration

C_∞ fluid phase equilibrium concentration

C(t) fluid phase concentration as function of time.

$\bar{C}(\tau)$ dimensionless fluid phase concentration as function of dimensionless time.

C_{o_2} fluid phase concentration of oxygen as a function of time.

$C_{o_2,0}$ initial fluid phase concentration of oxygen

$C_{o_2,\infty}$ fluid phase concentration of oxygen at equilibrium

D_{so} surface diffusivity coefficient at zero adsorbate loading

D_s surface diffusivity coefficient

D_p pore volume diffusivity coefficient

H oxygen isotherm constant,

K combined constant in reaction term

k_{LF} Langmuir Freundlich isotherm constant

k′ natural logarithm of the absicca intercept in the log-log plot of oxygen imbalance versus time,

k_{o2} reaction constant with respect to oxygen imbalance,

m reaction order with respect to adsorbate concentration,

M_t total amount of adsorbate which diffuses from the bulk phase

into the carbon particle at any time,t

M_∞ mass adsorbed at infinite time

k_{o_2} reaction order with respect to oxygen imbalance,

n Langmuir Freundlich isotherm constant

n′ reaction order with respect to oxygen imbalance,

n" negative of the slope of the log-log plot of normalised oxygen imbalance versus time

N adsorbate flux into the particle,

q_{os} adsorbate phase concentration in equilibrium with the initial fluid phase concentration,

$\bar{q}_\infty$ average adsorbate concentration at infinite time

$q(r,t)$ adsorbent phase concentration as a function of radial position and time

$\bar{q}(t)$ average adsorbate concentration on the particle as a function of time,t

$\bar{Q}(\tau)$ dimensionless average adsorbate concentration as a function of dimensionless time, $\bar{q}(t)/q_{os}$

$Q(\eta,\tau)$ dimensionless adsorbent phase concentration, $q(r,t)/q_{os}$

r radial coordinate,

r_s particle radius,

R reaction rate based on total volume of particle

t time

u uptake of adsorbent

V volume of the aqueous phase

W_s mass of the carbon particle

Greek alphabet

α solute distribution parameter (dimensionless), Wq_{os}/VC_o;

ε particle porosity,

Φ Thiele modulus

η dimensionless radius

λ initial surface loading, $\frac{q_o}{q_s}$

θ loading, $\frac{q}{q_s}$

ρ_p density of particle

τ dimensionless time

CHAPTER FOUR

COMBINED PORE AND SURFACE DIFFUSION IN PACKED BEDS

4.1 Introduction

Practical adsorption processes are in many cases associated with adsorption in a column. Adsorption particles are packed in a column and fluid containing one or more components flows through the bed.

An ideal plug flow system has no resistance to mass transfer. In such a system, the input concentration profile is replicated by the outlet response with a time delay corresponding to the hold-up in the column. In a real system, the outlet response is dispersed. The dispersion is the result of the combined effects of axial dispersion and mass transfer resistance. Information on the adsorption equilibrium are obtained from the time delay measurement while that on the sorption kinetics and extent of axial mixing are provided by measurement of the dispersion of the outlet response. To extract this information, the experimental response must be matched with the theoretical response curve, calculated from a suitable dynamic model for the system.

The consideration of the response of an initially sorbate free column to either a step change in sorbate concentration at the column inlet (step input) or to the injection of a small pulse of sorbate at the column inlet (pulse input) is a convenient way of studying the dynamics of a fixed bed adsorption column. The response to a step input is commonly called the

breakthrough curve while the pulse response is often referred to as the chromatographic response. The chromatographic response is a derivative of the breakthrough curve since a delta function (perfect pulse) is the derivative of the Heaviside function (perfect step) for a linear system. Practical convenience rather than fundamental theoretical consideration determines the choice of input function since exactly the same information may be derived from the response to either input.

In the course of the adsorption, a saturation zone is formed near the inlet of the column and a zone with increasing concentration is observed at the frontal part. A measurement of the effluent stream concentrations reveals a seepage of the adsorbable components when the mass transfer zone approaches the exit of the bed. This of course, gives the breakthrough curve. One convenient way of classifying adsorption systems is according to number of mass transfer zones in the dynamic response to a change in feed composition.

4.2 Literature Survey

In a fixed bed of adsorbent particles, the following mass transport processes are observed: axial dispersion in the intraparticle fluid phase, fluid to particle mass transfer, intraparticle diffusion (which may include surface, micropore and/or macropore diffusion), and a reversible adsorption in the interior of the particle.

Generally, the isotherms for organic compounds on activated carbons are non-linear and analytical solutions for breakthrough curves cannot be derived. Further, the adsorbers in this field are usually not long enough to

warrant the assumption of a constant pattern concentration profile which would simplify the calculation of the breakthrough curves.

Wilmanski, and Lipinski (1989) reported that the adsorption uptake in a column increases with increase in bed height and noticed that the effective pore diffusivity decreases during column performance. They observed that the breakthrough was achieved at the same throughput values (bed volumes), without regard to the superficial velocity used in the column tests at a given particle size fraction. These results provided sufficient assurance that the external mass transfer resistance could be neglected. The breakthrough curves for smaller particles were sharper than those for larger sizes. The number of bed volume (throughput) achieved prior to breakthrough was found to decrease with increasing carbon particle size in the bed at the different breakthrough criteria. Consequently, a higher GAC solid phase concentration can be achieved for the smaller carbon particle size used in the column. This is supported by the work of Goto et al. (1986). Reschke et al. (1986) reported that the reduction of particle size to one third the standard diameter resulted in a more than a three fold increase in diffusion time constant.

In past years various numerical techniques have been employed in solving the set of descriptive column equations. However, recently, the orthogonal collocation algorithm has become more commonly used rather than other methods, as it has been proved to be more time efficient. Raghavan and Ruthven (1983), showed that the orthogonal collocation method was far more time efficient than the exact solution in evaluating a breakthrough curve. They compared their numerical solution with the exact solution presented by Rasmusson and Neretnieks, (1980).

Crittenden et al. (1986) made a review of various models used in predicting the transport of organic compounds with saturated ground water flow. A detailed discussion of the dispersed flow, film transfer, pore and surface diffusion model (DFPSDM) was presented. The mechanisms accounted for in this model include (1) constant advective flow, (2) axial dispersion and diffusion, (3) film transfer resistance to mass transport from the mobile to the stationary phase, (4) local adsorption equilibrium between the solute in the intra-aggregate stagnant fluid and (5) both surface and pore diffusion as intra-stationary phase mass transport mechanisms.

4.3 Theoretical Model

Consider a column packed with activated carbon particles through which fluid stream containing concentration C(z,t) of an adsorbable species is flowing. We take an element of the bed and conduct a mass balance. If the flow pattern can be represented as axially dispersed plug flow, the differential fluid phase mass balance is:

$$-D_L \frac{\partial^2 C_b}{\partial z^2} + \frac{\partial}{\partial z}(\upsilon C_b) + \frac{\partial C_b}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial \bar{q}}{\partial t} = 0 \qquad (4.1)$$

The initial condition is

$$C_b\,(z > 0, t = 0) = 0 \qquad (4.2)$$

Boundary Conditions:

The boundary conditions are the Danckwerts (1953) boundary conditions. They are obtained by equating the mass flux entering and leaving the column.

$$v\left[C_I(t)-C_b\left(z=0^+,t\right)\right]=-D_L\frac{\partial C_b\left(z=0^+,t\right)}{\partial z} \tag{4.3}$$

$$\frac{\partial C_b\left(z=L,t\right)}{\partial z}=0 \tag{4.4}$$

The derivation of these boundary conditions is based on the assumption that the diffusion and dispersion occurs only within the column. Similarly , if the mass flux into the column is equated to the rate of accumulation of mass within the column, the following equivalent boundary conditions are obtained.

$$\begin{aligned} v\left[C_I(t)-C_b(z=L+,t)\right] = \frac{\partial}{\partial t}\int_o^L\Bigg[C_b(z,t)+\frac{3(1-\varepsilon)}{r_s^3\,\varepsilon} \\ .\int_o^{r_s}\left[\varepsilon_p C_p(r,z,t)+\rho_p q(r,z,t)\right]r^2\partial r\Bigg]\partial z \end{aligned} \tag{4.5}$$

Equation (4.4) is also the solution of the following boundary condition and its initial condition:

$$\frac{\partial^2 C_b\left(z=L,t\right)}{\partial t\;\partial z}=0;\quad \frac{\partial C_b\left(z=L,t=0\right)}{\partial z}=0 \tag{4.6}$$

Equations (4.5) and (4.6) are used in lieu of the Danckwerts boundary conditions in the numerical solutions of the model because they simplify the numerical method.

Mass transfer rates are often correlated in terms of an effective mass transfer coefficient k_f, defined according to a linear driving force equation.

$$\frac{\partial \bar{q}}{\partial t} = k_f a\left[C_b(z,t) - C_p(r = r_s, z, t)\right] = \frac{3k_f}{r_s}\left[C_b(z,t) - C_p(r = r_s, z, t)\right] \tag{4.7}$$

where a is the external surface area per unit particle ($3/r_s$ for spherical particles) and $\bar{q}$ is the adsorbed phase concentration averaged over a particle.

The fluid phase equations become:

$$\frac{\partial C_b(z,t)}{\partial t} = D_L \frac{\partial^2 C_b(z,t)}{\partial z^2} - v\frac{\partial C_b(z,t)}{\partial z} - \frac{3k_f(1-\varepsilon)}{\varepsilon r_s}\left[C_b(z,t) - C_p(r = r_s, z, t)\right] \tag{4.8}$$

The terms which appear in the equation account for accumulation in the mobile liquid phase, axial dispersion and diffusion, advective flow, and rate of transport from the mobile phase to the stationary phase by liquid phase mass transfer.

The particle equations are :

$$\varepsilon_p \frac{\partial C_p(r,z,t)}{\partial t} + \rho_p \frac{\partial q(r,z,t)}{\partial t} = \frac{1}{r_s^2}\left\{ r^2 \left[\varepsilon_p D_p \frac{\partial C_p(r,z,t)}{\partial r} + \rho_p D_s \frac{\partial q(r,z,t)}{\partial r} \right] \right\} \tag{4.9}$$

which can also be written as :

$$\varepsilon_p \frac{\partial C_p(r,z,t)}{\partial t} + \rho_p \frac{\partial q(r,z,t)}{\partial t} = \frac{1}{r_s^2}\left\{ r^2 \left[\varepsilon_p D_p \frac{\partial C_p}{\partial q} + \rho_p D_s \right] \frac{\partial q}{\partial r} \right\} \tag{4.10}$$

The initial conditions are :

$$C_p(r,z,t=0) = 0 \tag{4.11}$$

$$q(r,z,t=0) = 0 \tag{4.12}$$

Boundary conditions:

At the center, due to symmetry, we have :

$$\frac{\partial q(r=0,z,t)}{\partial r} = 0 \tag{4.13}$$

$$\frac{\partial C_p(r=0,z,t)}{\partial r} = 0 \tag{4.14}$$

At the surface,

$$k_f\left[C_b(z,t)-C_p(r=r_s,z,t)\right] = D_p\varepsilon_p\frac{\partial C_p(r=r_s,z,t)}{\partial r}+D_s\rho_p\frac{\partial q(r=r_s,z,t)}{\partial r} \qquad (4.15)$$

Equivalently, at the surface we have :

$$k_f r_s^2\left[C_b(z,t)-C_p(r=r_s,z,t)\right]= \frac{\partial}{\partial t}\int_0^{r_s}\left[\varepsilon_p C_p(r=r_s,z,t)+\rho_p q(r=r_s,z,t)\right]r^2\partial r \qquad (4.16)$$

In equation (4.15), the liquid phase mass flux from the fluid phase is equated to the flux at the surface of the particle. In equation (4.16), the rate of fluid phase mass transfer is equated to the accumulation of mass within the particles. Equation (4.16) is used in the numerical method as it simplifies the solution.

The fluid in the film around the particles is assumed to be in equilibrium with the adsorbed phase concentration on the surface of the particle. Thus, the fluid phase concentration is related to the adsorbed surface concentration by an adsorption equilibrium equation.

Table 4.1 : Dimensionless Groups in Column.

Dimensionless Group	Equation	Definition
Peclet number, Pe	$\frac{vL}{D_L}$	$\frac{\text{rate of transport by advection}}{\text{rate of transport by axial dispersion}}$
Stanton number, St	$\frac{k_f L(1-\varepsilon)}{r_s \varepsilon v}$	$\frac{\text{rate of transport by film transfer}}{\text{rate of transport by advection}}$
Surface diffusion modulus, Ed_s	$\frac{LD_s Dg_s}{vr_s^2}$	$\frac{\text{rate of transport by pore diffusion}}{\text{rate of transport by advection}}$
Pore diffusion modulus, Ed_p	$\frac{LD_p Dg_p}{vr_s^2}$	$\frac{\text{rate of transport by surface diffusion}}{\text{rate of transport by advection}}$
Particle diffusion modulus, Ed	$Ed_s + Ed_p$	$\frac{\text{rate of transport by intra-particle diffusion}}{\text{rate of transport by advection}}$
Adsorbed solute distribution ratio, Dg_s	$\frac{(1-\varepsilon)\varepsilon_p}{\varepsilon}$	$\frac{\text{mass of solute contained in immobile fluid}}{\text{mass of solute contained in the mobile phase evaluated at equilibrium with } C_o}$
Immobile fluid solute distribution ratio, Dg_p	$\frac{(1-\varepsilon)\rho_p q_e}{\varepsilon C_o}$	$\frac{\text{mass of adsorbate on the particle surface}}{\text{mass of solute contained in the mobile phase evaluated at equilibrium with } C_o}$
Solute distribution ratio, Dg	$Dg_p + Dg_s$	$\frac{\text{mass of adsorbate contained in the particle surface}}{\text{mass of solute contained in the mobile phase evaluated at equilibrium with } C_o}$
Throughput, T	$\frac{tv}{L(1+D_g)}$	$\frac{\text{mass of solute fed to the column}}{\text{mass of solute in a column saturated to capacity}}$

Dimensionless Form

Dimensionless variables used are:

$$\bar{z}=\frac{z}{L};\ \bar{C}_I=\frac{C_I}{C_o};\ \bar{r}=\frac{r}{r_s};\ \bar{C}=\frac{C}{C_o};\ \bar{q}=\frac{q}{q_e};$$

$$T=\frac{t\nu}{L\left(1-D_g\right)};\ \bar{X}(\bar{r},\bar{z},T)=X(r,z,tT)/X_e$$

Definitions :

$X(r,z,t$ is the particle concentration i.e. it includes the solute in the pore water and that adsorbed on the GAC particle surface as a function of radial and axial position and time. In equation form, it is given by:

$$X(r,z,t)=\varepsilon_p C_p(r,z,t)+\rho_p q(r,z,t) \qquad (4.17)$$

X_e is the particle concentration in equilibrium with C_o.

$$X_e=\varepsilon_p C_o+\rho_p q_e \qquad (4.18)$$

Equation (4.17) is converted to the dimensionless form as follows :

$$\bar{X}(\bar{r},\bar{z},T)=X(r,z,t)/X_e \quad \text{and} \quad \bar{q}=q/q_e$$

The various dimensionless groups used in the subsequent analysis are summarized in Table 1. From Table 1:

$$D_g = \frac{(1-\varepsilon)(\rho_p q_e + \varepsilon_p C_o)}{\varepsilon C_o} \doteq \frac{(1-\varepsilon)X_e}{\varepsilon C_o} \tag{4.19}$$

$$\overline{X}(\bar{r},\bar{z},T) = \frac{\varepsilon_p C_o \overline{C}_p(\bar{r},\bar{z},T)}{X_e} + \frac{\rho_p q_e \overline{q}(\bar{r},\bar{z},T)}{X_e}$$

$$\frac{Dg_s}{Dg} = \frac{(1-\varepsilon)\rho_p q_e}{\varepsilon C_o} \cdot \frac{\varepsilon C_o}{(1-\varepsilon)(\rho_p q_e + \varepsilon_p C_o)} = \frac{\rho_p q_e}{(\rho_p q_e + \varepsilon_p C_o)}$$

$$\frac{Dg_p}{Dg} = \frac{(1-\varepsilon)\varepsilon_p}{\varepsilon} \cdot \frac{\varepsilon C_o}{(1-\varepsilon)(\rho_p q_e + \varepsilon_p C_o)} = \frac{\varepsilon_p C_o}{(\rho_p q_e + \varepsilon_p C_o)}$$

Therefore,

$$\overline{X}(\bar{r},\bar{z},T) = \frac{Dg_p}{Dg}\overline{C}_p(\bar{r},\bar{z},T) + \frac{Dg_s}{Dg}\overline{q}(\bar{r},\bar{z},T) \tag{4.20}$$

We have :

$$\frac{\partial C_b}{\partial t} = \frac{C_o \nu}{L(1+D_g)}\frac{\partial \overline{C}_b}{\partial T}; \quad \frac{\partial C_b}{\partial z} = \frac{C_o}{L}\frac{\partial \overline{C}_b}{\partial \bar{z}} \text{ ; and } \quad \frac{\partial^2 C_b}{\partial z^2} = \frac{C_o}{L^2}\frac{\partial^2 \overline{C}_b}{\partial \bar{z}^2}$$

Therefore,

$$\frac{1}{(1+D_g)}\frac{\partial \overline{C}}{\partial T} = \frac{D_L}{\nu L}\frac{\partial^2 \overline{C}}{\partial \bar{z}^2} - \frac{\partial \overline{C}}{\partial \bar{z}} - \frac{3(1-\varepsilon)k_f L}{\varepsilon r_s \nu}\left[\overline{C}_b(\bar{z},T) - \overline{C}_p(1,\bar{z},T)\right]$$

$$\frac{1}{(1+D_g)}\frac{\partial \bar{C}}{\partial T}=\frac{1}{Pe}\frac{\partial^2 \bar{C}}{\partial \bar{z}^2}-\frac{\partial \bar{C}}{\partial \bar{z}}+3St\left[\bar{C}_b(\bar{z},T)-\bar{C}_p(1,\bar{z},T)\right] \qquad (4.21)$$

Equation (4.5) is converted to dimensionless form as follows :

$$\nu C_o\left[C_I(t)-C_b(z=1,T)\right] = \frac{\nu C_o}{L(D_g+1)}\frac{\partial}{\partial T}\int_o^l\left[\bar{C}_b(\bar{z},T)+\frac{3(1-\varepsilon)}{r_s^3\,\varepsilon}\right.$$
$$\left.\int_o^l\left[\bar{X}(\bar{r},\bar{z},T).X_e\right]\bar{r}^2 r_s^2\,\partial\bar{r}\right]L\,\partial\bar{z}$$

$$\left[C_I(t)-C_b(z=1,T)\right] = \frac{1}{(D_g+1)}\frac{\partial}{\partial T}\int_o^1\left[\bar{C}_b(\bar{z},T)+\right.$$
$$\left.\frac{3(1-\varepsilon)}{\varepsilon C_o}\left(\varepsilon_p C_o+\rho_p q_e\right).\int_o^1\bar{X}(\bar{r},\bar{z},T).\bar{r}^2\,\partial\bar{r}\right]\partial\bar{z}$$

This reduces to :

$$\left[C_I(t)-C_b(z=1,T)\right] = \frac{1}{(D_g+1)}.\frac{\partial}{\partial T}.$$
$$\int_o^1\left[\bar{C}_b(\bar{z},T)+3Dg\int_o^1\bar{X}(\bar{r},\bar{z},T).\bar{r}^2\,\partial\bar{r}\right]\partial\bar{z}$$

(4.22)

Initial condition:

$$\bar{C}_b\left[0<\bar{z}\le 1,T=0\right]=0 \qquad (4.23)$$

Boundary conditions:

$$\bar{C}_I(T) - \bar{C}_b(\bar{z}=1,T) = -\frac{1}{Pe}\frac{\partial \bar{C}_b(\bar{z}=0^+,T)}{\partial \bar{z}} \qquad (4.24)$$

$$\frac{\partial \bar{C}_b(\bar{z}=1,T)}{\partial \bar{z}} = 0 \qquad (4.25)$$

Dimensionless Form of Particle Equations :

Equation (4.9) is transformed as follows :

The left hand side becomes

$$\frac{\varepsilon_p C_o \nu}{L(D_g+1)}\frac{\partial \bar{C}_p}{\partial T} + \frac{\rho_p q_e \nu}{(D_g+1)}\frac{\partial \bar{q}}{\partial T} = \frac{\nu}{L(D_g+1)}\left[\varepsilon_p C_o \frac{\partial \bar{C}_p}{\partial T} + \rho_p q_e \frac{\partial \bar{q}}{\partial T}\right]$$

$$= \frac{\varepsilon_p C_o \nu}{LDg_p}\frac{D_g}{(D_g+1)}\frac{\partial \bar{X}(\bar{r},\bar{z},T)}{\partial T}$$

Equation (4.9) then reduces to:

$$\frac{D_g}{(D_g+1)}\frac{\partial \bar{X}(\bar{r},\bar{z},T)}{\partial T} = \frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\cdot \left\{\bar{r}^2\left[\frac{LDg_p}{\varepsilon_p C_o \nu}\cdot\frac{\varepsilon_p C_o D_p}{r_s^2}\frac{\partial \bar{C}_p}{\partial \bar{r}} + \frac{D_s \rho_p q_e}{r_s^2}\cdot\frac{\varepsilon_p C_o D_p}{r_s^2}\frac{\partial \bar{q}}{\partial \bar{r}}\right]\right\}$$

We note the following :

$$Ed_s + \frac{Dg_p}{Dg_s} Ed_s = \frac{LD_s}{\nu r_s^2}\left[Dg_s + Dg_p\right],$$

$$Ed_s - \frac{Dg_p}{Dg_s} Ed_s = \frac{LDg_p}{\nu r_s^2}\left[D_p - D_s\right],$$

and, from the definition of X (r,z,t),

$$\frac{\partial \bar{q}(\bar{r},\bar{z},T)}{\partial \bar{r}} = \frac{Dg}{Dg_s}\frac{\partial \bar{X}}{\partial \bar{r}} - \frac{Dg_p}{Dg_s}\frac{\partial \bar{C}_p}{\partial \bar{r}}$$

The term in the bracket in equation (4.9), then becomes :

$$Ed_s \frac{\partial \bar{C}_p}{\partial \bar{r}} + \frac{LDg_p}{r_s^2 \nu}\cdot\left\{\frac{D_s \rho_p q_e}{\varepsilon_p C_o}\frac{D_g}{Dg_s}\frac{\partial \bar{X}}{\partial \bar{r}} - D_s \frac{\rho_p q_e}{\varepsilon_p C_o}\frac{Dg_p}{Dg_s}\frac{\partial \bar{C}_p}{\partial \bar{r}}\right\}$$
$$= \left(Ed_p - \frac{Dg_p}{Dg_s}Ed_s\right)\frac{\partial \bar{C}_p(\bar{r},\bar{z},T)}{\partial \bar{r}} + \left(Ed_s + \frac{Dg_p}{Dg_s}Ed_s\right)\frac{\partial \bar{X}(\bar{r},\bar{z},T)}{\partial \bar{r}}$$

Equation (4.9) then becomes:

$$\frac{D_g}{(D_g+1)}\frac{\partial \bar{X}(\bar{r},\bar{z},T)}{\partial T} = \frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\cdot$$
$$\left\{\bar{r}^2\left[\left(Ed_p - \frac{Dg_p}{Dg_s}Ed_s\right)\frac{\partial \bar{C}_p(\bar{r},\bar{z},T)}{\partial \bar{r}} + \left(Ed_s + \frac{Dg_p}{Dg_s}Ed_s\right)\frac{\partial \bar{X}(\bar{r},\bar{z},T)}{\partial \bar{r}}\right]\right\}$$

(4.26)

Initial conditions become:

$$\bar{C}_p(\bar{r},\bar{z},T=0)=0 \tag{4.27}$$

$$\bar{q}(\bar{r},\bar{z},T=0)=0 \tag{4.28}$$

Boundary conditions becomes:

At the center,

$$\frac{\partial \bar{q}(\bar{r}=0,\bar{z},T)}{\partial \bar{r}}=0 \tag{4.29}$$

$$\frac{\partial \bar{C}_p(\bar{r}=0,\bar{z},T)}{\partial r}=0 \tag{4.30}$$

At the surface of the particle, the boundary conditions transforms as follows :

$$k_f r_s^2 C_o\left[\bar{C}_b(\bar{z},T)-\bar{C}_p(\bar{r}=r_s,\bar{z},T)\right] = \frac{\nu}{L(1+D_g)} r_s^3 X_e \frac{\partial}{\partial T}\int_o^1 \bar{X}(\bar{r},\bar{z},T)\bar{r}^2\partial\bar{r}$$

We note that

$$X_e=\varepsilon_p C_o+\rho_p q_e = \frac{\varepsilon C_o}{(1-\varepsilon)} Dg$$

Hence,

$$\left(\frac{k_f L(1-\varepsilon)}{r_s \varepsilon v}\right).\left(\frac{1+D_g}{Dg}\right)\left[\bar{C}_b(\bar{z},T)-\bar{C}_p(\bar{r}=r_s,\bar{z},T)\right] = \frac{\partial}{\partial T}\int_o^1 \bar{X}(\bar{r},\bar{z},T)\bar{r}^2\partial\bar{r}$$

Or,

$$St.\left(\frac{1+D_g}{Dg}\right)\left[\bar{C}_b(\bar{z},T)-\bar{C}_p(\bar{r}=r_s,\bar{z},T)\right] = \frac{\partial}{\partial T}\int_o^1 \bar{X}(\bar{r},\bar{z},T)\bar{r}^2\partial\bar{r} \qquad (4.31)$$

The dispersion coefficient was calculated using the correlation given in Ruthven (1978)

$$D_L = \delta_1 D_M + \delta_2 d_p v \qquad (4.32)$$

where $\delta_1 = 0.7; \delta_2 = 0.5$

v = interstitial velocity,

d_p = particle density

The following equation (Wakao and Funzkri) was used to calculate the film transfer coefficient. The correlation is valid for Reynolds number between 3 and 1000.

$$\frac{2k_f r}{D_M} = 2 + 1.1R^{0.6}Sc^{0.333} \qquad (4.33)$$

Where k_f is the liquid - phase mass transfer coefficient, R is Reynolds number, and Sc is Schmidt number. The dimensionless groups are defined as follows:

$$Sc = \frac{\mu}{\rho_l D_M} \tag{4.34}$$

$$R = \frac{2 \rho_l r v}{\mu} \tag{4.35}$$

where , μ is viscosity of water (9.8E-4 kg.s/m), ρ_l is density of water (997.8 kg/m^3), r is mean radius of adsorbent particle, v is the superficial velocity (3.286E-3 m/s) , and D_M is the diffusivity of the adsorbate in water calculated using the Wilke - Chang equation . The values of D_M and r were presented in chapter two.

Solution Scheme

Equations (21) and (26) were coupled by assuming local equilibrium at the surface of the carbon particle. The isotherm equation was used to relate the surface and pore concentrations within the immobile phase by equation (20).

Equations (4.20) to (4.30) represents a set of simultaneous, nonlinear, partial differential equations (PDEs) that can be solved numerically by orthogonal collocation (OC) (Finlayson, 1980). The orthogonal collocation method converts the set of PDEs to a set of linear polynomials. The dependence of concentration on position within the particles and column is now represented by linear combination of orthogonal polynomials. These polynomials are used in integration and differentiation algorithms that only require values for the dependent variables, concentration, at specific collocation points. The collocation points are located at the roots of the polynomials where the polynomials approximations agree exactly with the true values of the dependent variables. The PDEs are converted to a series of ordinary differential equations (ODEs) which describe the temporal variation of the dependent variable at the collocation points.

Applying OC to the equations yields the following MC ODEs for the mobile phase in the axial direction:

$$\frac{d\bar{C}_b(k,T)}{dT} = (Dg+1)\sum_{i=1}^{MC}\left[\frac{B_{i,k}{}^{z}}{Pe} - A_{i,k}{}^{z}\right]\bar{C}_b(k,T) - 3(Dg+1)St\left[\bar{C}_b(k,T) - \bar{C}_p(NC,k,T)\right] \qquad (4.36)$$

for k = 2 to MC -1

$$\frac{d\bar{C}_b(k=1,T)}{dT}=\left\{\left[(Dg+1)\left[\bar{C}_I(T)-\bar{C}_b(MC,T)\right]-\sum_{k=2}^{MC-1}\left(W_k^z-W_{MC}^z\frac{A_{MC,k}^z}{A_{MC,MC}^z}\right)\frac{d\bar{C}_b(k,T)}{dT}\right]\cdot\left(W_1^z-W_{MC}^z\frac{A_{MC,1}^z}{A_{MC,MC}^z}\right)^{-1}\right\}-\left\{\left[3Dg\left(\sum_{k=1}^{MC}W_k^z\left(\sum_{j=1}^{NC}W_j^r\frac{d\bar{X}(j,k,T)}{dT}\right)\right)\right]\cdot\left(W_1^z-W_{MC}^z\frac{A_{MC,1}^z}{A_{MC,MC}^z}\right)^{-1}\right\} \tag{4.37}$$

$$\frac{d\bar{C}_b(MC,T)}{dT}=-\sum_{k=1}^{MC-1}\frac{A_{MC,k}^z}{A_{MC,MC}^z}\frac{d\bar{C}_b(k,T)}{dT} \tag{4.38}$$

The entrance condition (equation (4.37) was derived by the simultaneous solution of the ODEs that result from the application of OC to (4.23) to (4.25). The initial conditions for the bulk solution concentration at axial locations k = 1 to MC are

$$\bar{C}_b(k,T=0)=0 \tag{4.39}$$

Time- variable influent concentrations are utilized in (4.37) by using $\bar{C}_I(T)$ for the influent concentration as a function of time.

Applying OC to (4.26) and (4.31) gives the following set of ODEs at NC collocation points in the immobile phase:

$$\frac{d\bar{X}(NC,k,T)}{dT} = \frac{(Dg+1)}{Dg}\sum_{i=1}^{NC}\left[\left(\left(Ed_p - \frac{Dg_p}{Dg_s}Ed_s\right)St\left[\bar{C}_b(k,T) - \right]\right.\right.$$
$$\left.\left. .B^r_{i,j}\bar{C}_p(i,k,T) + \left(Ed_s + \frac{Dg_p}{Dg_s}Ed_s\right)B^r_{i,j}\bar{X}(i,k,T)\right]\right. \qquad (4.40)$$

for j = 1 to NC-1 and k = 1 to MC.

$$\frac{d\bar{X}(NC,k,T)}{dT} = \frac{(Dg+1)}{Dg\,W^r_{NC}}St\left[\bar{C}_b(k,T) - \bar{C}_p(NC,k,T)\right]$$
$$- \sum_{j=1}^{NC-1}\frac{W^r_j}{W^r_{NC}}\frac{d\bar{X}(j,k,T)}{dT} \qquad (4.41)$$

for k = 1 to MC

Equations (4.300 is satisfied by using symmetrical orthogonal polynomials to represent the spatial derivatives.

The initial conditions for the surface and pore concentrations at axial locations k = 1 to MC are:

$$\bar{X}(j,k,T=0) = 0; \qquad \bar{C}_p(j,k,T=0) \qquad (4.42)$$

The OC method was applied to (4.20) as follows :

$$\bar{X}(j,k,T)=\frac{Dg_p}{Dg}\bar{C}_p(j,k,T)+\frac{Dg_s}{Dg}\left(\frac{K_{LF}\bar{C}_o\bar{C}_p(j,k,T)^{1/N_{LF}}}{1+K_{LF}\bar{C}_o\bar{C}_p(j,k,T)^{1/N_{LF}}}\right) \qquad (4.43)$$

$A^z_{i,k}$, $B^z_{i,k}$ and W^z_i are the OC matrices and vector that are used to approximate the first derivatives, the second derivative, and the integral of relative concentration with respect to axial position, respectively. These were derived using unsymmetric jacobi polynomials with weighting factors of $(1 - x^2)$. $B^z_{i,k}$ and W^z_i are the OC matrix and vector that approximate the second derivatives and the integral in the radial direction using symmetric Legendre polynomials (Villadsen and Michelsen, 1978).

The ODEs were solved using an algorithm called IVPAG, from the IMSL package. The system of ODEs were solved by first solving (4.43) for $\bar{C}_p(j,k,T)$. Next, the various derivatives were evaluated in this order : equations (4.40), (4.41), (4.36) , (4.38), and (4.37). This was done starting with initial conditions given in equations (4.39) and (4.42) and the time-variable influent concentration given in equation (4.37).

The above algorithm has been used, tested and proved highly efficient by Crittenden et al (1986). The accuracy of the program used was attested by reproducing the results of Crittenden et al. (1986).

4.4 Results And Discussion

The column parameters and their values are presented in the Tables 4.2 and 4.3 below:

Table 4.2 : Column Parameters

Column Parameters	Value
Influent Concentration, C_o	70 mg/L
Temperature	21 °C
Column length, L	60 cm
Particle density, ρ_p	0.67E6 mg/L
Interstitial velocity, v	0.8418 cm/s
Bed porosity, ε	0.39
Particle porosity, ε_p	0.63
Film transfer coefficient, k_f	phenol -3.88E-3cm^2/s o-cresol - 3.60E-3cm^2/s
Dispersion coefficent, D_L	phenol - 6.657 cm^2/s o-cresol - 6.657 cm^2/s

Table 4.3 : Program Input for column system.

Program Input		
Dim. groups / Parameters	Phenol	o-cresol
Pe	769.2	769.2
St	5.545	5.1449
$fs = \frac{Dg_s}{Dg}$	0.99925	0.99965
Ed	2.486	2.0583
K_{LF}	0.1345	0.1353
n_{LF}	3.125	3.448

The program was used to fit the data by Abuzaid (1993). The program was found to sensitive to the value of Station number used which in turn depends on the value of the film transfer coefficient. The correlation used in predicting the film transfer coefficient affects the value to some extent. This was shown in the work by Abuzaid (1993).

The fits are presented in Figures 4.1 and 4.2. The experimental effluent concentration data did not rise up to the inlet concentration as expected. Consequently, the experimental values were more reliably predicted at the earlier portion of the plots than at the later.

4.5 Conclusions and Recommendations.

The pore and surface diffusion model for a column was done. The model parameters used are those determined in chapter two of this work. The fits obtained predicted the experimental data favorably well at low reduced effluent concentration than at higher values. The discrepancies was noted to be due to the difficulty encountered in purging the column completely of oxygen before the experiment.

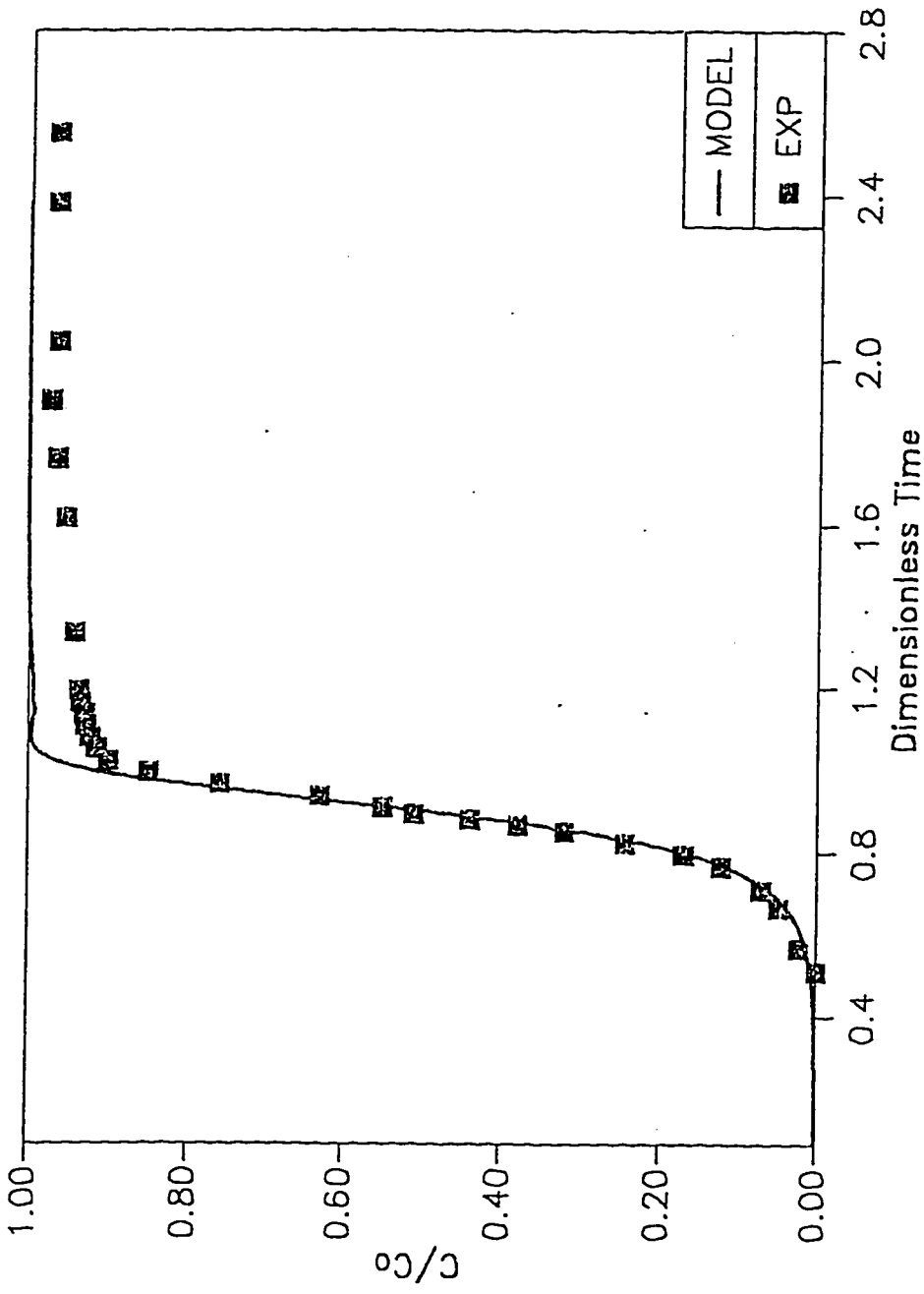

Fig 4.1: Predicted and Experimental Breakthrough Curves
Adsorption of o-cresol in column at 294K

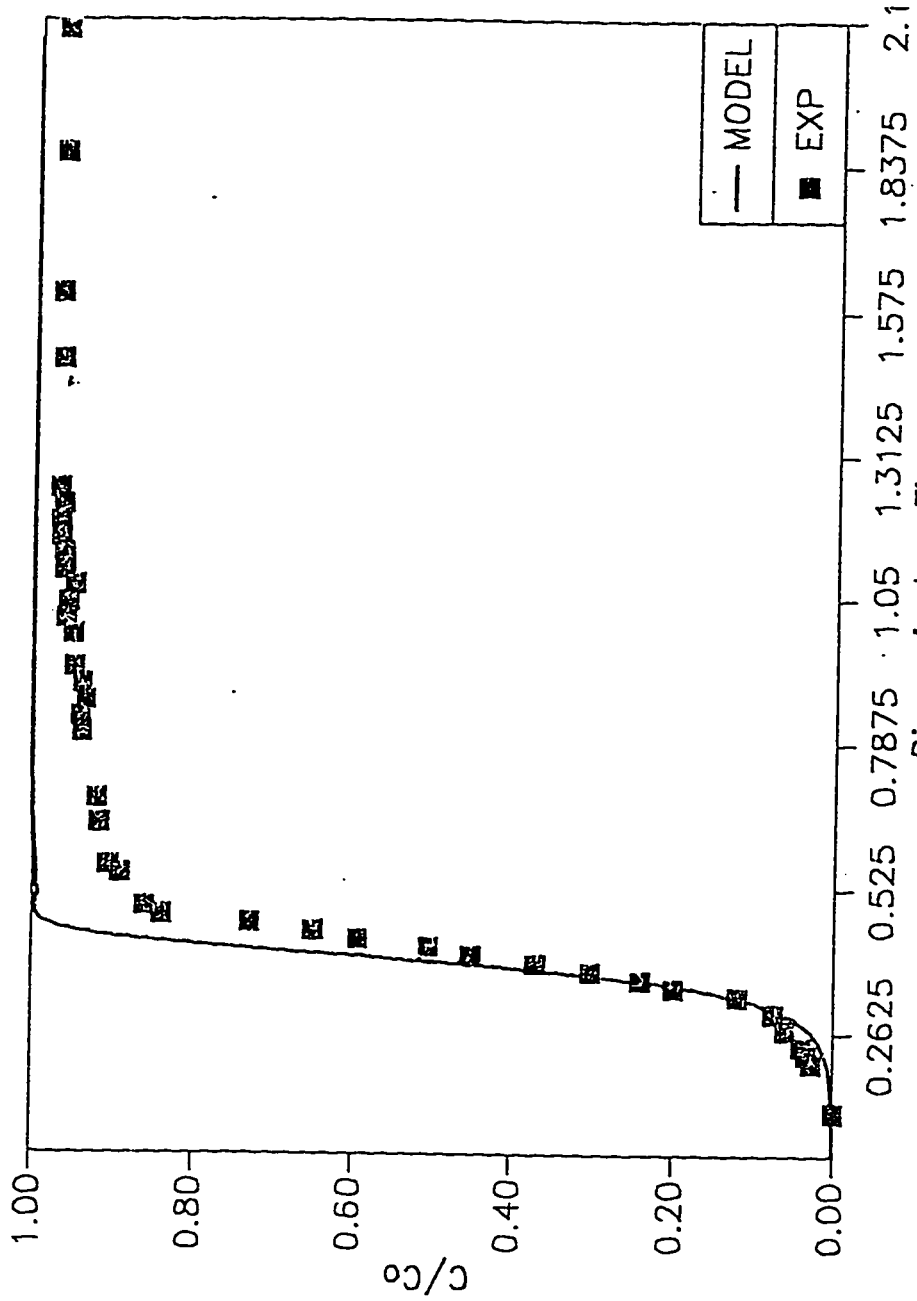

Fig.4.2: Predicted and Experimental Breakthrough Curves Adsorption of phenol in columns at 294K

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4.7 Nomenclature

A	column cross sectional area (L^2)
$A_{i,k}^{z}$	orthogonal collocation matrix that approximates the first derivative in the axial direction.
Bi_p	pore diffusion Biot number, ratio of the external liquid phase mass transfer rate to the pore diffusion rate within the particle, equal to $(1-\varepsilon)k_f r_s / (\varepsilon D_p Dg_p)$ (dimensionless)
Bi_s	surface diffusion Biot number, ratio of the external liquid phase mass transfer rate to the surface diffusion rate within the particle equal to $(1-\varepsilon)k_f r_s / (\varepsilon D_s Dg_s)$ (dimensionless)
$B_{i,j}^{r}$	orthogonal collocation matrix that approximates the Laplacian quadrature in radial direction
$B_{i,k}^{z}$	orthogonal collocation matrix that approximates the Laplacian quadrature in axial direction
$C_b(z,t)$	bulk fluid phase concentration in mobile phase as a function of axial position and time (M/L^3)
$\overline{C}_b(\bar{z},T)$	$\overline{C}_b(z,t) / C_o$ (dimensionless)
$\overline{C}_I(T)$	$C_I(T) / C_o$ (dimensionless)
C_o	arbitrary concentration used to normalize dimensionless equations, usually the maximum influent concentration (M/L^3)

$C_p(r,z,T)$ $C_p(r,z,T)/C_o$ (dimensionless)

Dg solute distribution ratio, the ratio of the mass of adsorbate contained in the particle phase to the mass of solute contained in the mobile phase evaluated at equilibrium with C_o equal to $Dg_p + Dg_s$ (dimensionless).

Dg_p immobile fluid solute distribution ratio, the ratio of the mass of solute contained in immobile fluid to the mass of solute contained in the mobile phase evaluated at equilibrium with C_o equal to $(1-\varepsilon)\varepsilon_p / \varepsilon$ (dimensionless)

Dg_s adsorbed solute distribution ratio, the ratio of the mass of adsorbate on the soil surface to the mass of solute contained in the mobile phase evaluated at equilibrium with C_o, equal to $(1-\varepsilon)\rho_p q_e / (\varepsilon C_o)$ (dimensionless)

D_M molecular diffusion coefficient of Phenol in water, (L^2/t)

D_L axial dispersion and diffusion coefficient, (L^2/t)

D_p pore diffusion coefficient, equal to D_M / τ_p , (L^2/t)

D_s surface diffusion coefficient (L^2/t)

Ed particle diffusion modulus, the ratio of the rate of mass transfer due to diffusion within the particle to the rate of mass transfer due to advection, equal $Ed_p + Ed_s$ (dimensionless)

Ed_p pore diffusion modulus, the ratio of the of mass transfer due to pore diffusion within the particle to the rate of mass due to

advection, equal to LD_pDg_p / vr_s^2 (dimensionless)

Ed_s surface diffusion modulus, the ratio of the of mass transfer due to surface diffusion within the particle to the rate of mass due to advection, equal to LD_sDg_s / vr_s^2 (dimensionless)

k_f film transfer coefficient (L / t)

K_{LF} Langmuir Freundlich isotherm constant, $(L^3/M)^{1/n}$

L length of column (L)

MC number of collocation points in the axial direction.

MTZ mass transfer zone

n Langmuir Freundlich isotherm constant (dimensionless)

NC number of collocation points in radial direction

Pe Peclet number, equal to vL / D_L (dimensionless)

Q flow rate (L^3 / t)

$q(r, z, t)$ particle phase concentration as a function of radial and axial position and time (M/M)

q_e particle phase concentration in equilibrium with C_o, (M/M)

r_s radius of particle, (L)

Re Reynolds number, (dimensionless)

St Stanton number, the ratio of the mass transfer due to external liquid phase mass transfer to the mass transfer due to advection, equal to $(1-\varepsilon)k_fL / (\varepsilon vr_s)$ (dimensionless)

T throughput, the ratio of mass of solute fed to the column to the mass of solute in a column saturated to capacity, equal to

	$tv / L\left(1 + D_g\right)$ (dimensionless)
t	elapsed time (t)
v	v_s/ε, average interstitial velocity in pores (L/t)
v_s	specific discharge, equal to Q/A (L/t)
W_j^r	orthogonal collocation vector that approximates the Gauss quadrature in the radial direction.
W_i^z	orthogonal collocation vector that approximates the Gauss quadrature in the axial direction.
$X(r, z, t)$	particle concentration including solute pore water and adsorbed on particle surface as a function of radial and axial position and time, equal to $\varepsilon_p C_p(r,z,t) + \rho_p q(r,z,t)\ \left(M / L^3\right)$
X_e	particle concentration in equilibrium with C_o , $\varepsilon_p C_o + \rho_p q_e, \left(M / L^3\right)$
$\overline{X}(\bar{r}, \bar{z}, T)$	$\overline{X}(r,z,t) / X_e$ (dimensionless)
z	axial direction (L)
$\bar{z}$	z/L (dimensionless)
ε	void fraction of column filled b mobile fluid (dimensionless)
ε_p	void fraction of particle (dimensionless)
μ	fluid viscosity (M/Lt)
ρ_p	particle density, $\left(M / L^3\right)$
τ_p	tortuosity (dimensionless)

CHAPTER FIVE

COMBINED PORE AND SURFACE DIFFUSION WITH REACTION IN PACKED BEDS

5.1 Introduction

Adsorption with reaction studies are usually conducted in batch systems. Practical cases, however, are conducted in packed columns. The adsorption of phenol with reaction conducted in columns exhibits similar characteristics as the batch reactor studies. The principal characteristics have been already discussed in chapter three of this work.

5.2 Literature Survey

Vidic and Suidan (1992) studied the influence of dissolved oxygen on the breakthrough curve for o-cresol. They observed that the size of GAC particles and the initial o-cresol concentration had no detectable influence on either the aerobic and anaerobic adsorption isotherms. There was no biological activity in the isotherm bottles and Freundlich isotherm gave a good fit. The increase in adsorption uptake due to the presence of dissolved oxygen ranges from 22% to 200%. The oxidative coupling reaction accounted for the increase in adsorption uptake. This phenomenon was used to explain the characteristics tail observed in the breakthrough curves for o-cresol reported by Liu and Weber, (1981); Peel and Benedek (1981) and, Seidel and Gelbin (1986).

Abuzaid (1993) conducted parametric studies of the adsorption of phenol, and o-cresol on GAC under the influence of dissolved oxygen in both batch and column systems. The influence of dissolved oxygen level, temperature and

pressure were emphasised. When the adsorption temperature, pH and dissolved oxygen level are fixed, the uptake increases directly with the mass of the GAC used .The uptake increases directly with increase in dissolved oxygen concentration. This fact was noted in the batch studies. The increase in uptake was shown to be the result of the oxidative coupling reactions occurring primarily on the surface of the GAC particles. The uptake for phenol, o-cresol and nitrophenol at 1mg/L under aerobic conditions were respectively 163%, 114%, and 18% higher than the anaerobic uptakes. The reaction, plausibly catalysed by the GAC, takes place between the physisorbed sorbate and chemisorbed oxygen molecules. The products of the reaction were identified as 2,2-dihydroxyl-1, 1-biphenyl, 4-phenoxyphenol and a phenolic trimer. The oxidative coupling reaction is favoured by high temperature and pH (Abuzaid, 1993; Grant and King, 1990; Cooney and Xi, 1992).

Abuzaid (1993) conducted desorption studies to access the reversibility of the adsorption. The recovery efficiencies observed for the anaerobic and aerobic cases were respectively 70% and 23%. The reduction in recovery in the aerobic test is attributed partly to the oxidative coupling reaction occurring on the GAC during the adsorption process. This is supported by the earlier work of Grant and King (1990).

5.3 Theoretical Model

The general descriptive equation are similar to that of the case of adsorption without reaction as presented in section 4.3 of chapter four. The only difference however, is in the particle equation which now includes a reaction term. The initial and boundary conditions are exactly the same.

The general particle equation now becomes

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{ r^2 \left[\varepsilon_p D_p \frac{\partial C_p}{\partial r} + \rho_p D_{so} \frac{n}{1-\bar{q}\lambda} \frac{\partial q}{\partial r} \right] \right\} - R \qquad (5.1)$$

where R is the reaction term.

In dimensionless form , we have

$$\frac{Dg}{(Dg+1)} \frac{\partial \bar{X}}{\partial T} = \frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\left\{ \bar{r}^2 \left[\left(Ed_p - \frac{Dg_p}{Dg_s} \frac{Ed_{so}.n}{1-\lambda\bar{q}} \right) \frac{\partial \bar{C}_p}{\partial \bar{r}} + \left(1 + \frac{Dg_p}{Dg_s} \right) \left(\frac{Ed_{so}.n}{1-\lambda\bar{X}} \right) \frac{\partial \bar{X}}{\partial \bar{r}} \right] \right\} - \frac{Dg_p L}{\varepsilon_p \nu C_o} R \qquad (5.2)$$

The reaction term R, as defined in chapter three is

$$R = k_{o_2} k_{phe} q_e^m \bar{q}^m \left(q_{o_2} - q_{o_2,\infty} \right)^n \qquad (5.3)$$

A plot of the normalised oxygen concentration decay against time on a log - log basis gave a straight line. The log - log relationship was of the form:

$$\log_e \left(\frac{C_{o_2} - C_{o_2,\infty}}{C_{o_2,0} - C_{o_2,\infty}} \right) = \log_e k - n'' \log_e t \qquad (5.4)$$

where the negative of b is the slope of the plot and natural log of k is the intercept. This reduces to the following :

$$\frac{q_{o_2} - q_{o_2,\infty}}{q_{o_2,0} - q_{o_2,\infty}} = \frac{C_{o_2} - C_{o_2,\infty}}{C_{o_2,0} - C_{o_2,\infty}} = kt^{-n''} \qquad (5.5)$$

The throughput which is the dimensionless time in this case is defined as

$$T = \frac{t\nu}{L(Dg+1)} \tag{5.6}$$

Therefore,

$$t = \frac{TL(Dg+1)}{\nu} = \sigma T \tag{5.7}$$

where

$$\sigma = \frac{L(Dg+1)}{\nu}$$

We assume a linear isotherm for the oxygen, i.e.

$$q_{o_2} = HC_{o_2} \tag{5.8}$$

Therefore, we have the following ;

$$q_{o_2} - q_{o_2,\infty} = H\left(C_{o_2,0} - C_{o_2,\infty}\right)kt^{-n''}$$

or

$$q_{o_2} - q_{o_2,\infty} = H\left(C_{o_2,0} - C_{o_2,\infty}\right)k\sigma^{-n''}t^{-n''} \tag{5.9}$$

The reaction term becomes:

$$R = k_{phe}\, k_{o_2}\, q_e^m \left[H\left(C_{o_2,0} - C_{o_2,\infty}\right)k\sigma^{-n''}T^{-n''}\right]^{n'} \bar{q}^m$$

$$R = \left\{ k_{phe} k_{o_2} \, q_e^m \left[H\left(C_{o_2,0} - C_{o_2,\infty}\right) k\sigma^{-n''} \right]^{n'} \right\} \bar{q}^m \; T^{-n''n'} \tag{5.10}$$

Let,

$$K = k_{phe} k_{o_2} \, q_e^m \left[H\left(C_{o_2,0} - C_{o_2,\infty}\right) k\sigma^{-n''} \right]^{n'} \tag{5.11}$$

The value of n' is assumed to be one. Thus, the reaction rate expression becomes :

$$R = K \bar{q}^m \; T^{-n''} \tag{5.12}$$

The overall particle equation then becomes ;

$$\frac{Dg}{(Dg+1)} \frac{\partial \bar{X}}{\partial T} = \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left\{ \bar{r}^2 \left[\left(Ed_p - \frac{Dg_p}{Dg_s} \frac{Ed_{so} n}{1 - \bar{X}\lambda} \right) \frac{\partial \bar{C}_p}{\partial \bar{r}} + \left(1 + \frac{Dg_p}{Dg_s} \right) \left(\frac{Ed_{so} n}{1 - \bar{X}\lambda} \right) \frac{\partial \bar{X}}{\partial \bar{r}} \right] \right\} - \frac{Dg_p I K}{\varepsilon_p \nu C_o} T^{-n'} \bar{q}^m \tag{5.13}$$

The reaction rate is rearranged as follows to facilitate the calculation of the value of the rate constant, K in the particle equation above

$$R = \left[k_{phe} k_{o_2} \left(C_{o_2,0} - C_{o_2,\infty} \right) q_e^m H k \right] \sigma^{-n''} T^{-n''} \bar{q}^m \tag{5.14}$$

The overall rate constants determined in chapter three were given as :

$$K_b = \left[k_{phe} k_{o_2} \left(C_{o_2,0} - C_{o_2,\infty} \right) q_e^m H k \right] \left[\frac{r_s^2}{q_{os} D_{os}} \right] \left[\frac{r_s^2}{D_{os}} \right]^{-n''} \tag{5.15}$$

$$K_c = K_b q_{os} \left[\frac{r_s^2}{D_{os}} \right]^{1-n''} \tag{5.16}$$

$$K = K_c \sigma^{-n''} \tag{5.17}$$

The set of descriptive PDEs were converted to a system of ODEs and solved by orthogonal collocation method as described in chapter four. The boundary conditions and initial conditions are unchanged. The particle equation, however is replaced by equation (5.13) to account for the reaction occurring in the particle.

5.4 Results And Discussion.

All other parameters and program input are as presented in chapter four. The only additional parameters are reaction constants. The overall reaction rate calculated as described above are given in Table 5.1. The fits for phenol and o-cresol are shown in Figures 5.1 to 5.4. The RMS values for the fits were in the range of 0.33 - 0.4. The fits for the first order and second order cases were almost identical. The same observation was made in the batch systems.

The fits are general good at the earlier portion of the curve, but deviate more from the experimental readings as the dimensionless concentration tends to unity. This observation may be due to either of two reasons. First, there may be experimental error associated with the difficulty of ensuring accurate measurement

Table 5.1 : Reaction orders and overall constants for column systems

	n = 0.6	n = 0.6
	order = 1	order = 2
K (phenol)	4.06E-2	9.22E-2
K (o-cresol)	7.68E-2	1.24E-1

of oxygen concentration in the system. Secondly, there may be the problem of oxygen diffusion which is not accounted for by the present reaction model in column systems. Generally, the quality of fits obtained in the batch systems are better than those of the column systems. This is probably due to the fact that in the experimental set-up in the in the column systems there continued to be an input of dissolved oxygen into the system. whereas in the batch system the oxygen was consumed.

5.5 Conclusions and Recommendations.

The adsorption of phenol and its reaction with dissolved oxygen was modelled. The reaction constants used were obtained from the results got in the batch studies. The fits obtained, though representative of the general trend of the experimental data, are not good enough. There is a need to investigate the reaction process separately in a column and devise a more appropriate reaction model.

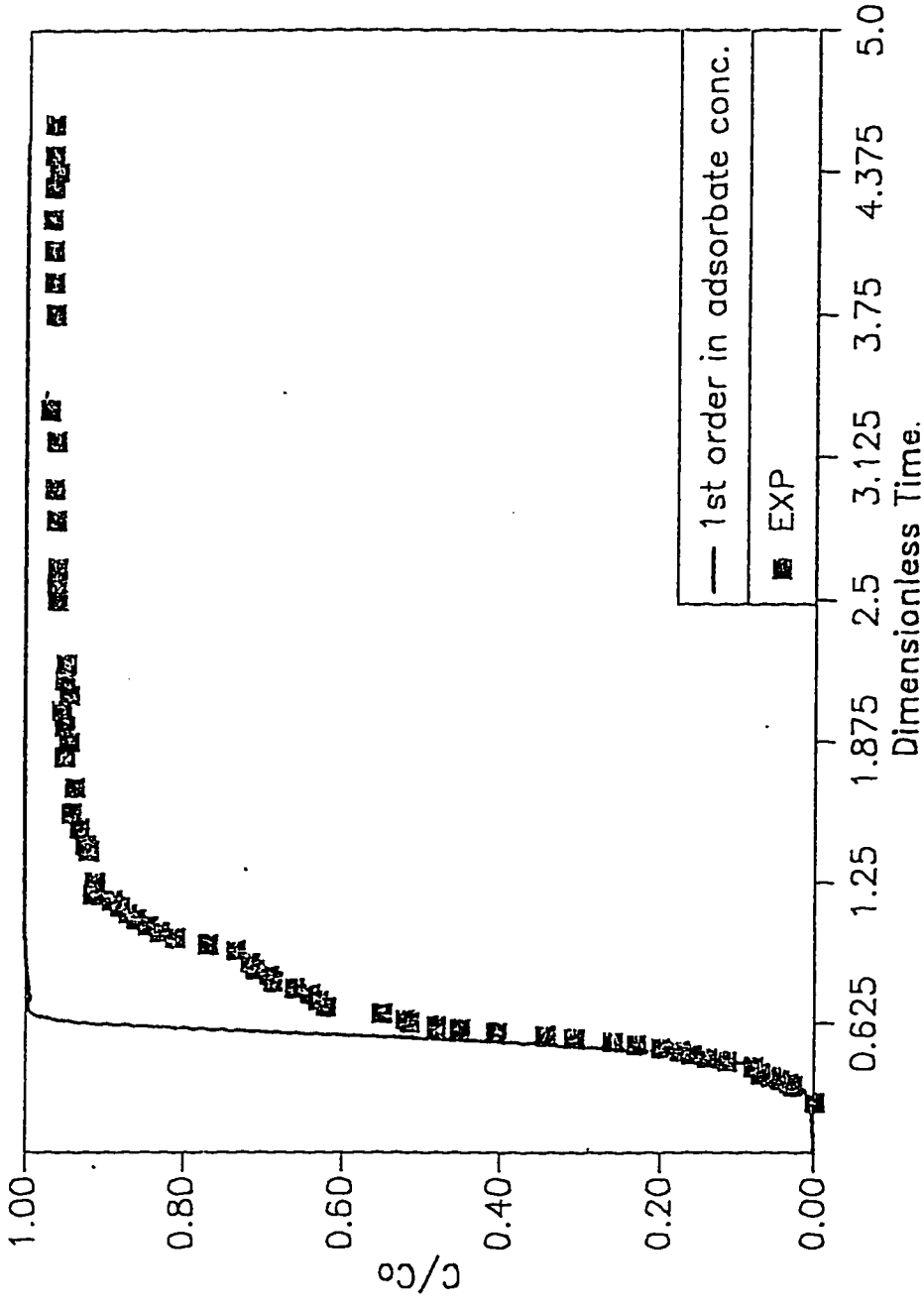

Fig 5.1: Predicted and Experimental Breakthrough Curves
Adsorption with Reaction of phenol in column at 294K.(1st order)

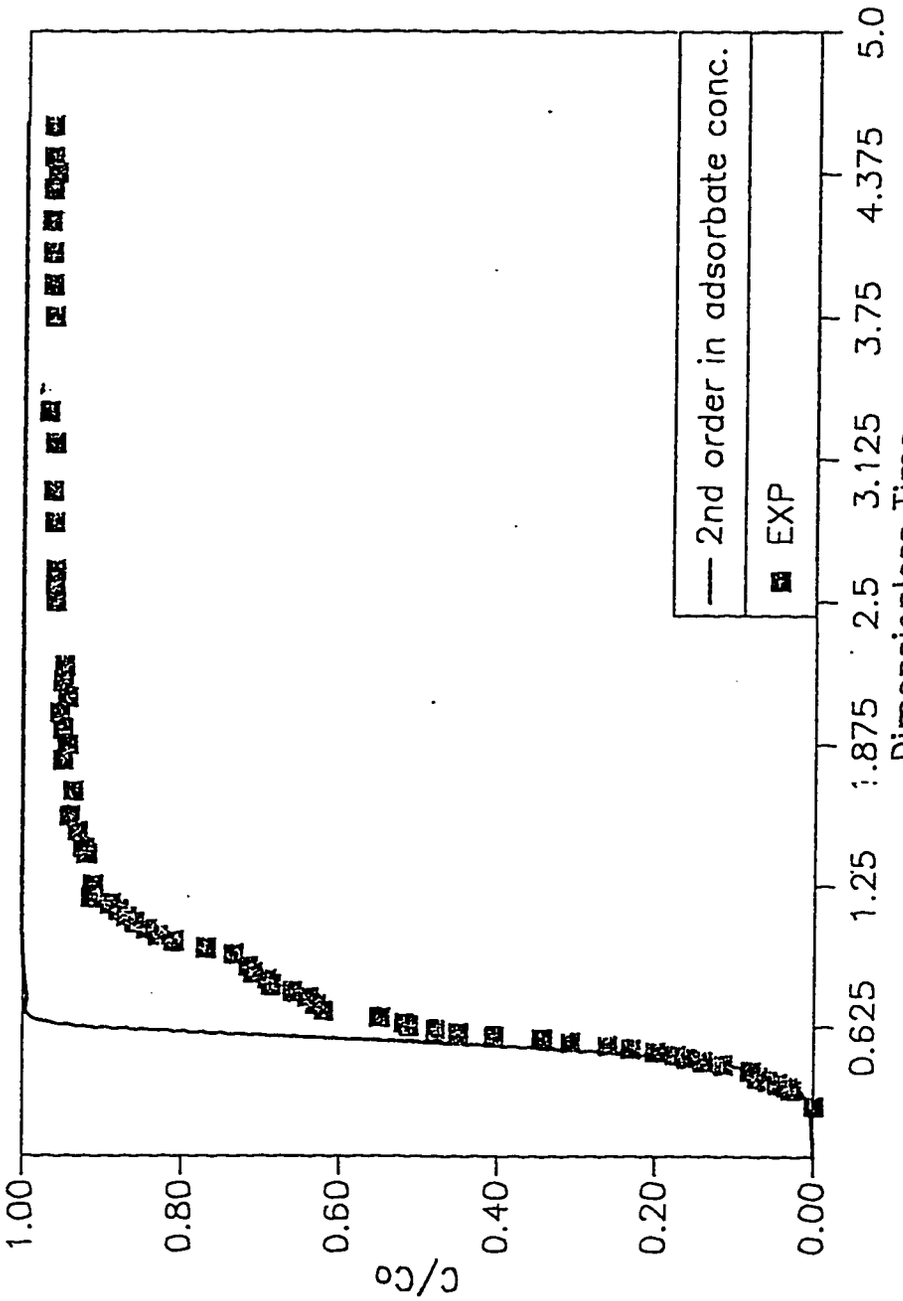

Fig 5.2: Predicted and Experimental Breakthrough Curves
Adsorption with Reaction of Phenol in column at 294K. (2nd order)

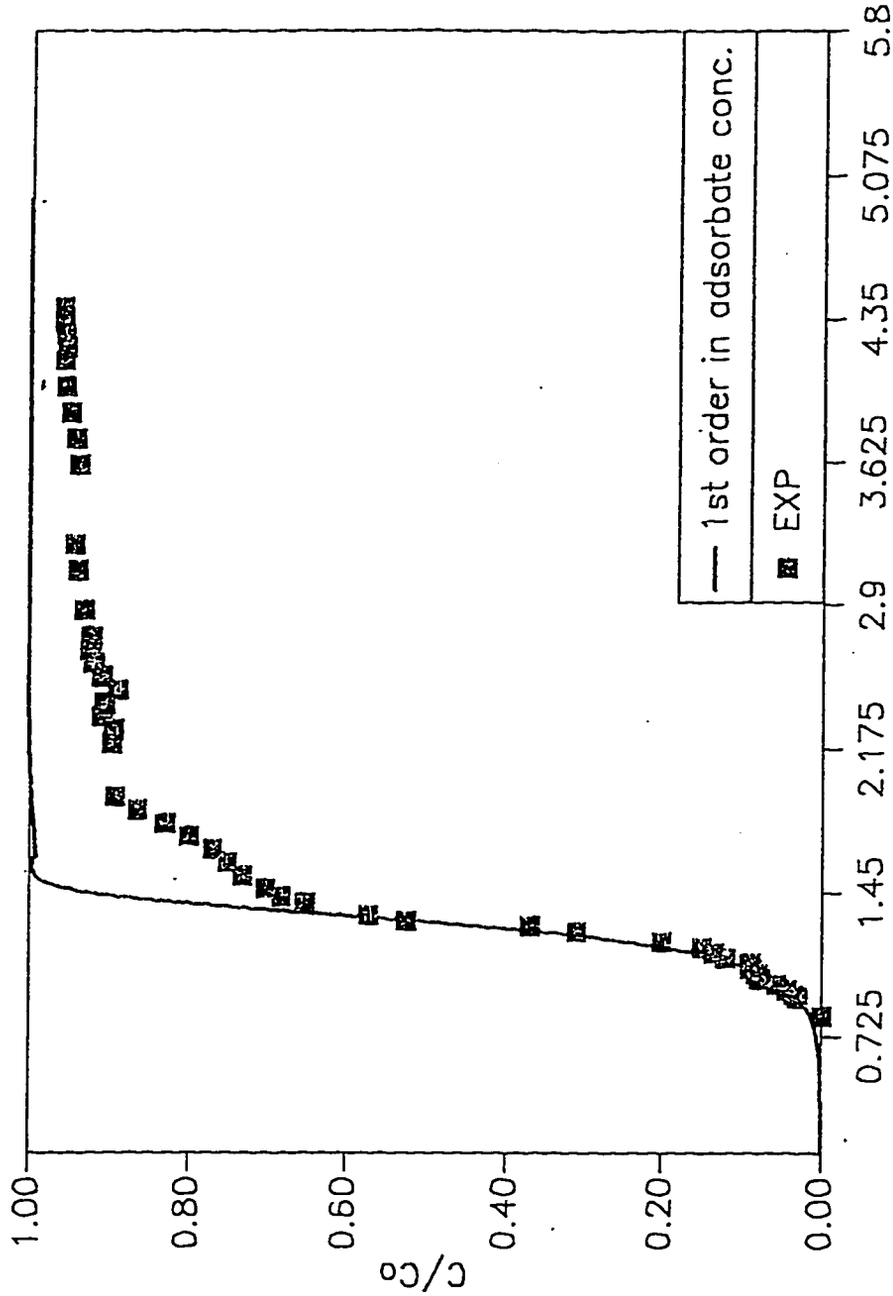

Fig 5.3:Predicted and Experimental Breakthrough Curves
Adsorption with Reaction of o- cresol at 294K. (1st order)

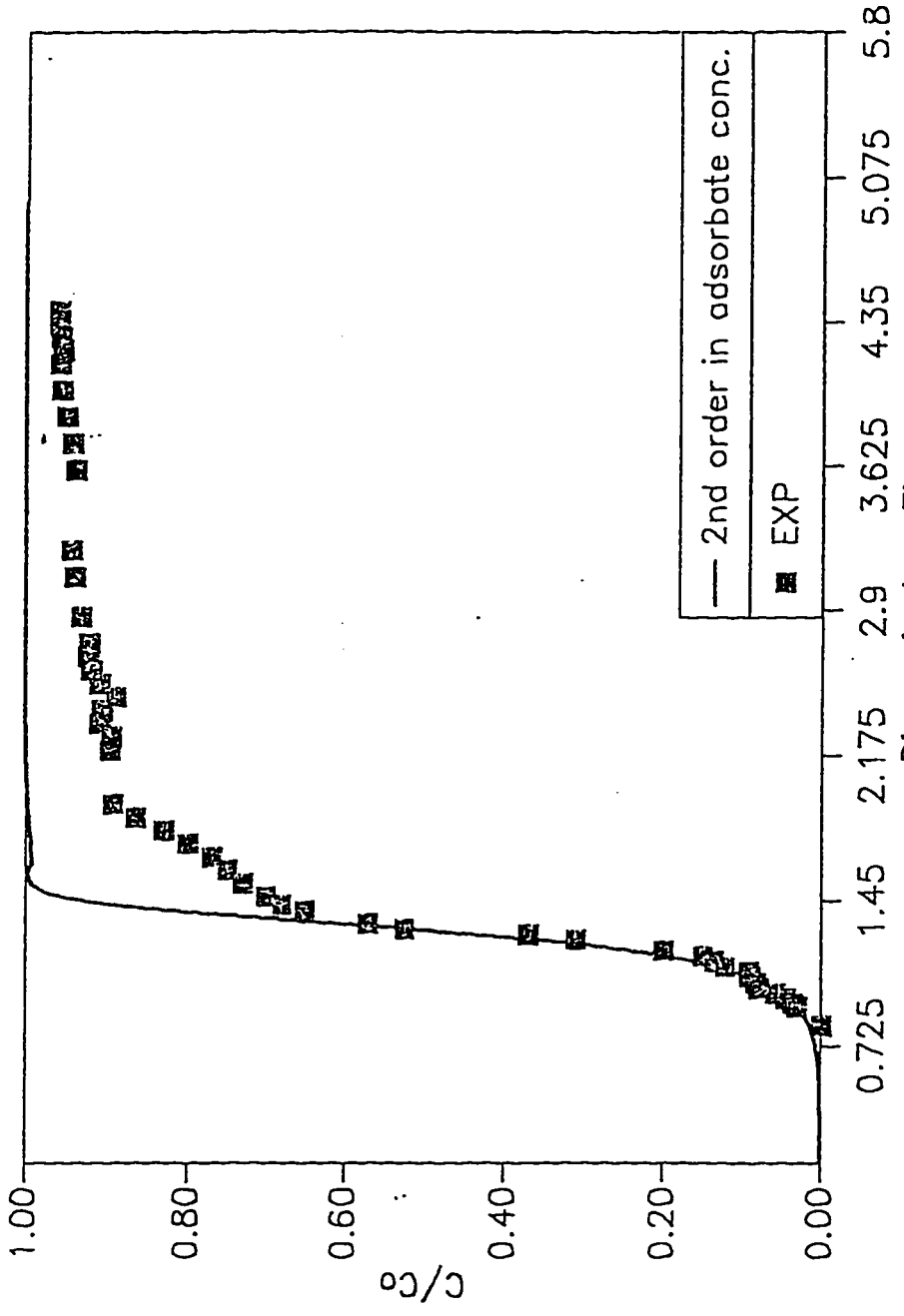

Fig 5.4: Predicted and Experimental Breakthrough Curves. Adsorption with Reaction of o-cresol at 294K.(2nd order)

5.6 Literature Cited

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CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

(1) The adsorption of phenol on granular activated carbon (GAC) was effectively modeled using five different models. The models used are the pore diffusion model (PDM), the homogeneous surface diffusion model (HSDM) with constant D_s, the HSDM but accounting for the variation of D_s with adsorbed phase concentration , the pore and surface diffusion model (PSDM) with constant D_s , and the PSDM but accounting for the variation of D_s for the adsorbed phase concentration.

(2) The PDM proved to be grossly inadequate in predicting the adsorption process when the concentration level of the data is high (1000mg/L)

(3) The HSDM and PSDM fits were almost identical indicating that the pore diffusion contribution is only significant at the early part of the process and it exerts a notable influence on the shape of D_s versus time plot.

(4) The variation of D_s with time is significant. However, the influence of this variation on the overall fit is not conspicuous. Hence, compensation for D_s by Darken's relation, though significant on its own, was only slightly reflected in the curves.

(5) The reaction of phenol with dissolved oxygen at the surface of the GAC was successfully modeled. On final analysis, the best rate form was first order in adsorbed phase concentration and -0.6 order in reaction time.

(6) The actual order with respect to oxygen imbalance was assumed to be 1. There were insufficient data to determine this. The reaction mechanism presented, though plausible, is purely speculative. Actual mechanism and order in oxygen imbalances can only be obtained from further studies with objectives focused on these needs.

(7) The column fits were generally poor. The data were adequately modeled at low reduced concentrations, but at high reduced concentrations (0.86-1.0), there exist some irreconcilable discrepancies. These were attributed to the difficulties experienced in handling the dissolved oxygen during the experimental work as this is continually added to the system during the column studies whereas it diminishes during the batch operation.

Recommendations

(1) Further experimental investigation is needed to truly certify the reaction mechanism and order of the oxygen imbalance.

(2) The influence of the diffusion of oxygen should be investigated in the column by the inclusion of an equation that will account for the diffusion of oxygen .

APPENDICES

Appendix A1

Program for Pore and Surface Diffusion in Batch Systems

FILE: CRANK6N FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
*************************************************************************** CRA00010
*                          APPENDIX A1                                    * CRA00020
*   PROGRAM FOR PORE AND SURFACE DIFFUSION IN BATCH SYSTEMS               * CRA00030
*                                                                         * CRA00040
*************************************************************************** CRA00050
*                                                                           CRA00060
      PROGRAM CRANK6                                                       CRA00070
*                                                                          CRA00080
* LAGMUIR FREUNDLICH ISOTHERM : GENERAL PROGRAM FOR PORE AND SURFACE       CRA00090
* DIFFUSION MODEL AND SURFACE DIFFUSION MODEL WITH PROVISION MADE FOR      CRA00100
* ACCOUNTING FOR CONCENTRATION DEPENDENCE VIA DARKEN'S RELATION.           CRA00110
*                                                                          CRA00120
*                                                                          CRA00130
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                CRA00140
      DOUBLE PRECISION KF,NF,LAMBDA                                        CRA00150
      PARAMETER(N=51,M=1000,NEXP=15)                                       CRA00160
      DIMENSION Q(N,0:M),QNEW(N),QOLD(N),QAVG(0:M),QMID(N),                CRA00170
     / CBAR(0:M),TAU(0:M),A(N),B(N),C(N),D(N),                             CRA00180
     / CCAL(NEXP), TEXP(NEXP),CEXP(NEXP),ETAU(NEXP),DSCAL(NEXP),           CRA00190
     / CTAU(NEXP), SQTAU(NEXP), UPCAL(NEXP),UPEXP(NEXP)                    CRA00200
      COMMON /INEXP/TEXP,CEXP                                              CRA00210
      COMMON /INDATA1/EP,QS,DP,DS,KF,CEOCO,RS,NF                           CRA00220
      COMMON /INDATA2/RHOP,CO,TEMP                                         CRA00230
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                    CRA00240
      EXTERNAL AVERAGE,THOMAS,LOAD,INTER,POLATE,INITIA,OUTPUT              CRA00250
                                                                           CRA00260
      CALL INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,             CRA00270
     /             Q,QMID, QAVG,CBAR )                                     CRA00280
                                                                           CRA00290
      X = DS/DP                                                            CRA00300
                                                                           CRA00310
*** GENERAL LOOP                                                          CRA00320
                                                                           CRA00330
      DO 400 J = 0, M-1                                                    CRA00340
      ITER1 = 0                                                            CRA00350
      ITER2 = 0                                                            CRA00360
      TAU(J) = REAL(J)*DTAU                                                CRA00370
  399 CONTINUE                                                             CRA00380
      DO 20  I = 1, N                                                      CRA00390
   20 QOLD(I)  = Q(I,J)                                                    CRA00400
      IF ( ITER1 .EQ. 0) THEN                                              CRA00410
                                                                           CRA00420
      QAVG(J+1) = QAVG(J) + EPSI1                                          CRA00430
      CHECK = EPSI1                                                        CRA00440
      ELSE                                                                 CRA00450
                                                                           CRA00460
      CALL AVERAGE ( N,QNEW,DR,QAV )                                       CRA00470
      CHECK = ABS ( QAVG(J+1) - QAV )                                      CRA00480
      QAVG(J+1) = QAV                                                      CRA00490
                                                                           CRA00500
      ENDIF                                                                CRA00510
                                                                           CRA00520
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                                 CRA00530
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/                  CRA00540
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )                  CRA00550
```

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```
                                                                      CRA00560
      QNNEW    = Q(N,J+1)                                             CRA00570
                                                                      CRA00580
      IF ( ITER2 .EQ. 0 ) THEN                                        CRA00590
                                                                      CRA00600
      DO 30 I = 1 , N                                                 CRA00610
 30   QMID(I) = QMID(I) + EPSI2*(I)                                   CRA00620
      ELSE                                                            CRA00630
      DO 40 I = 1 , N                                                 CRA00640
 40   QMID(I) = ( Q(I,J) + Q(I,J+1) )/ 2.0D0                          CRA00650
      ENDIF                                                           CRA00660
                                                                      CRA00670
      ITER1 = ITER1 + 1                                               CRA00680
      ITER2 = ITER2 + 1                                               CRA00690
                                                                      CRA00700
      CALL LOAD ( X,N,DTAU,DR,LAMBDA,QOLD,QMID,QNNEW,A,B,C,D )        CRA00710
      CALL THOMAS ( N,A,B,C,D,QNEW )                                  CRA00720
                                                                      CRA00730
      DO 50 I = 1, N                                                  CRA00740
      Q(I,J+1) = QNEW(I)                                              CRA00750
 50   CONTINUE                                                        CRA00760
                                                                      CRA00770
      IF  ( (CHECK .GT. ERROR ) .AND. ( ITER1 .LT. 50) ) GOTO 399     CRA00780
                                                                      CRA00790
C     PRINT17, TAU(J), CBAR(J)                                        CRA00800
C  17 FORMAT(2X,E15.8,2X,E15.8 )                                      CRA00810
                                                                      CRA00820
 400  CONTINUE                                                        CRA00830
      CALL POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,           CRA00840
     /             CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)            CRA00850
                                                                      CRA00860
      CALL INTER(M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,CEXP,CTAU,DSCAL)     CRA00870
      CALL OUTPUT(NEXP,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)   CRA00880
                                                                      CRA00890
      END                                                             CRA00900
                                                                      CRA00910
*****************************************************************   CRA00920
                                                                      CRA00930
      SUBROUTINE THOMAS ( N,A,B,C,D,X)                                CRA00940
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                           CRA00950
*************************************************************       CRA00960
* THOMAS ALGORYITHM FOR SOLVING A TRIDIAGONAL MATRIX         *       CRA00970
*************************************************************       CRA00980
                                                                      CRA00990
      PARAMETER( M =100)                                              CRA01000
      DIMENSION A(N),B(N),C(N),D(N),X(N),GAM(M),BET(M)                CRA01010
                                                                      CRA01020
      BET(1) = B(1)                                                   CRA01030
      GAM(1) = D(1)/B(1)                                              CRA01040
      DO 320 I = 2, N                                                 CRA01050
      BET(I) = B(I) -  A(I)*C(I-1)/BET(I-1)                           CRA01060
      GAM(I) = ( D(I) - A(I)*GAM(I-1) )/BET(I)                        CRA01070
 320  CONTINUE                                                        CRA01080
      X(N) = GAM(N)                                                   CRA01090
      DO 330 I = N -1,1,-1                                            CRA01100
```

```
C      CB = C(I)/BET(I)                                                  CRA01110
C      X(I) = GAM(I) - CB*X(I+1)                                         CRA01120
       X(I) = GAM(I) - C(I)*X(I+1)/BET(I)                                CRA01130
 330   CONTINUE                                                          CRA01140
                                                                         CRA01150
       RETURN                                                            CRA01160
       END                                                               CRA01170
                                                                         CRA01180
*****************************************************************************CRA01190
                                                                         CRA01200
       SUBROUTINE AVERAGE( N,Q,DR,QAVG)                                  CRA01210
* INTEGRATION VIA SIMPSON'S COMPOSITE RULE                               CRA01220
* RETURNS THE AVERAGE VALUE OF THE SOLID PHASE CONCENTRATION             CRA01230
                                                                         CRA01240
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               CRA01250
       DIMENSION Q(N)                                                    CRA01260
                                                                         CRA01270
       XI0 = Q(1)*0.0*0.0 +  Q(N)*1.0*1.0                                CRA01280
       XI1 = 0.0D0                                                       CRA01290
       XI2 = 0.0D0                                                       CRA01300
       DO 350  I = 2, N-1                                                CRA01310
       IF ( MOD(I,2) .EQ. 0 ) THEN                                       CRA01320
       XI2 = XI2 + Q(I)*( (DR*REAL(I-1))**2 )                            CRA01330
       ELSE                                                              CRA01340
       XI1 = XI1 + Q(I)*( (DR*REAL(I-1))**2 )                            CRA01350
       ENDIF                                                             CRA01360
  350  CONTINUE                                                          CRA01370
       XI = (DR/3.0D0)*( XI0  + 4.0D0*XI2 + 2.0D0*XI1 )                  CRA01380
       QAVG = 3.0D0*XI                                                   CRA01390
                                                                         CRA01400
       RETURN                                                            CRA01410
       END                                                               CRA01420
                                                                         CRA01430
*****************************************************************************CRA01440
       SUBROUTINE LOAD ( X,N,DTAU,DR,LAMBDA,QOLD,QMID,QNNEW,A,B,C,D )    CRA01450
*                                                                        CRA01460
*THIS PROGRAM CALCULATES THE VALUES OF A,B,C AND D REQUIRED IN THOMAS    CRA01470
* ALGORYTHM.                                                            CRA01480
*                                                                        CRA01490
       IMPLICIT DOUBLE PRECISION ( A-H,O-Z)                              CRA01500
       DOUBLE PRECISION KF,NF,LAMBDA                                     CRA01510
       COMMON /INDATA1/EP,QS,DP,DS,KF,CEOCO,RS,NF                        CRA01520
       COMMON /INDATA2/RHOP,CO,TEMP                                      CRA01530
       PARAMETER ( M =100 )                                              CRA01540
       DIMENSION QOLD(N),QMID(N),A(M),B(M),C(M),D(M),P(M),F(M),OMEGA(M), CRA01550
     /           PO(M)                                                   CRA01560
                                                                         CRA01570
       PHI = DTAU/DR**2                                                  CRA01580
       NM1 = N-1                                                         CRA01590
       PSI = EP/RHOP                                                     CRA01600
                                                                         CRA01610
       DO 10 I = 1, N                                                    CRA01620
       IF ( QMID(I) .GT. 1.0 ) THEN                                      CRA01630
       QMID(I) = 0.999990D0                                              CRA01640
       ELSE                                                              CRA01650
```

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```
      ENDIF                                                              CRA01660
      QL = LAMBDA*QMID(I)                                                CRA01670
      IF ( ( QMID(I) .EQ. 0.0).OR.(QL .LT. 1.0E-75) ) THEN               CRA01680
      DCDQ = (NF/(KF**NF)/QS)                                            CRA01690
      ELSE                                                               CRA01700
      DCDQ = (NF/(KF**NF)/QS)*(QL**(NF-1.0))/((1.0-QL)**(NF+1.0))        CRA01710
      ENDIF                                                              CRA01720
                                                                         CRA01730
** FOR HSDM CONSTANT DS MODEL :                                         CRA01740
C     PO(I)  =  X                                                        CRA01750
** FOR HSDM CONCENTRATION DEPEDENT DS MODEL :                           CRA01760
C     PO(I)  = PSI*DCDQ + X                                              CRA01770
** FOR PSD CONSTANT DS MODEL :                                          CRA01780
      PO(I)  =  X*NF/(1.0 - QL)                                          CRA01790
** FOR PSD CONCENTRATION DEPEDENT DS MODEL :                            CRA01800
C      PO(I)  = PSI*DCDQ + X*NF/(1.0 - QL)                               CRA01810
                                                                         CRA01820
   10 CONTINUE                                                           CRA01830
                                                                         CRA01840
      DO 20 I = 2, NM1                                                   CRA01850
      F(I) =(PHI/4.0D0)*(2.0D0*PO(I)/DBLE(I-1)+(PO(I+1)-PO(I-1))/2.0D0 )CRA01860
   20 CONTINUE                                                           CRA01870
*                                                                        CRA01880
* BOUNDARY NODE 1                                                       CRA01890
*                                                                        CRA01900
      A(1) = 0.0                                                         CRA01910
      B(1) = 1.0D0 + 3.0D0*PHI*PO(1)                                     CRA01920
      C(1) = - 3.0D0*PHI*PO(1)                                           CRA01930
      D(1) =( 2.0D0 - B(1))*QOLD(1) - C(1)*QOLD(2)                       CRA01940
*                                                                        CRA01950
* INTERIOR NODES 2 TO NM1                                               CRA01960
*                                                                        CRA01970
      DO 30 I = 2, NM1                                                   CRA01980
      A(I) = -PHI*PO(I)/2.0D0 + F(I)                                     CRA01990
      B(I) = 1.0D0 + PHI*PO(I)                                           CRA02000
      C(I) = -PHI*PO(I)/2.0D0 - F(I)                                     CRA02010
      D(I) = -A(I)*QOLD(I-1)+(2.0-B(I))*QOLD(I)- C(I)*QOLD(I+1)          CRA02020
  30  CONTINUE                                                           CRA02030
*                                                                        CRA02040
* BOUNDARY NODE N                                                       CRA02050
*                                                                        CRA02060
      A(N) = 0.0                                                         CRA02070
      B(N) = 1.0D0                                                       CRA02080
      C(N) = 0.0                                                         CRA02090
      D(N) = QNNEW                                                       CRA02100
                                                                         CRA02110
      RETURN                                                             CRA02120
      END                                                                CRA02130
                                                                         CRA02140
**********************************************************************   CRA02150
                                                                         CRA02160
      SUBROUTINE INTER ( M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,                CRA02170
     /                   CEXP,CTAU,DSCAL)                                CRA02180
**********************************************************************   CRA02190
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY.                  CRA02200
```

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```
* THE DIFFUSIVITY COEFFICIENT IS CALCULATED FROM THE        *          CRA02210
* RELATION : DSCAL = TAU*RS*RS/TIME                         *          CRA02220
*                                                           *          CRA02230
*************************************************************          CRA02240
*                                                                      CRA02250
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                            CRA02260
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),CTAU(NEXP),       CRA02270
     /          DSCAL(NEXP)                                           CRA02280
                                                                       CRA02290
      DO 100 IEXP = 2, NEXP                                            CRA02300
*                                                                      CRA02310
* SCAN THROUGH THE DATA                                               CRA02320
*                                                                      CRA02330
      ISCAN = 0                                                        CRA02340
   10 CONTINUE                                                         CRA02350
      ISCAN = ISCAN + 1                                                CRA02360
      IF ( CEXP(IEXP) .LT. CBAR(ISCAN) ) GOTO 10                       CRA02370
*                                                                      CRA02380
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                       CRA02390
*                                                                      CRA02400
      CTAU(IEXP) = ( TAU(ISCAN) - TAU(ISCAN+1) ) .                     CRA02410
     /             *( ( CEXP(IEXP) - CBAR(ISCAN+1))/                  CRA02420
     /             (CBAR(ISCAN)-CBAR(ISCAN+1))) + TAU(ISCAN+1)        CRA02430
      DPCAL = CTAU(IEXP)*RS*RS/( TEXP(IEXP)*60.0**2)                   CRA02440
      DSCAL(IEXP) = DPCAL*X                                            CRA02450
                                                                       CRA02460
  100 CONTINUE                                                         CRA02470
                                                                       CRA02480
      RETURN                                                           CRA02490
      END                                                              CRA02500
                                                                       CRA02510
*************************************************************************CRA02520
                                                                       CRA02530
      SUBROUTINE POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,      CRA02540
     /                   CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)        CRA02550
                                                                       CRA02560
*************************************************************          CRA02570
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY AND             CRA02580
* CALCULATES THE ROOT MEAN SQUARE OF THE DEVIATIONS OF                CRA02590
* PREDICTED CONCENTRATION VALUES FROM EXPERIMENTAL VALUES             CRA02600
*************************************************************          CRA02610
*                                                                      CRA02620
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                            CRA02630
      PARAMETER ( N = 20 )                                             CRA02640
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),SQTAU(N),         CRA02650
     /          ETAU(N),CCAL(N),UPCAL(N),UPEXP(N)                     CRA02660
                                                                       CRA02670
      DO 10 I = 1, NEXP                                                CRA02680
      ETAU(I) = DP*TEXP(I)*60.0**2/RS**2                               CRA02690
   10 CONTINUE                                                         CRA02700
                                                                       CRA02710
      RMS = 0.0                                                        CRA02720
      RMS2 = 0.0                                                       CRA02730
                                                                       CRA02740
      DO 100 I = 2, NEXP                                               CRA02750
```

```
      ISCAN = 0                                                          CRA02760
   20 CONTINUE                                                           CRA02770
      ISCAN = ISCAN + 1                                                  CRA02780
      IF ( ETAU(I) .GT. TAU(ISCAN) ) GOTO 20                             CRA02790
*                                                                        CRA02800
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                          CRA02810
*                                                                        CRA02820
      CCAL(I)=(CBAR(ISCAN)-CBAR(ISCAN+1))*((ETAU(IEXP)-TAU(ISCAN))/      CRA02830
     /        (TAU(ISCAN) - TAU(ISCAN+1))) + CBAR(ISCAN+1)               CRA02840
                                                                         CRA02850
      IF ( I .NE. 1 ) THEN                                               CRA02860
      RMS2 = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS2                     CRA02870
      ELSE                                                               CRA02880
      ENDIF                                                              CRA02890
      RMS = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS                       CRA02900
                                                                         CRA02910
      SQTAU(I) = SQRT( ETAU(I) )                                         CRA02920
      UPCAL(I) = ABS(1.0 - CCAL(I) )/( 1.0 - CEOCO )                     CRA02930
      UPEXP(I) = ABS(1.0 - CEXP(I) )/( 1.0 - CEOCO )                     CRA02940
                                                                         CRA02950
  100 CONTINUE                                                           CRA02960
                                                                         CRA02970
      RMS = 100.0*SQRT(RMS/REAL(NEXP))                                   CRA02980
      RMS2 = 100.0*SQRT(RMS2/REAL(NEXP-1))                               CRA02990
      DSFIT = DP*X                                                       CRA03000
                                                                         CRA03010
      RETURN                                                             CRA03020
      END                                                                CRA03030
                                                                         CRA03040
*************************************************************************CRA03050
      BLOCK DATA                                                         CRA03060
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                               CRA03070
      DOUBLE PRECISION KF,NF                                             CRA03080
      PARAMETER ( N =15 )                                                CRA03090
      DIMENSION TEXP(N), CEXP(N)                                         CRA03100
      COMMON /INDATA1/EP,QS,DP,DS,KF,CEOCO,RS,NF                         CRA03110
      COMMON /INDATA2/RHOP,CO,TEMP                                       CRA03120
      COMMON /INEXP/TEXP,CEXP                                            CRA03130
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                  CRA03140
                                                                         CRA03150
      DATA EPSI1, EPSI2, ERROR / 1.0D-8,1.0D-9,1.0D-13/                  CRA03160
      DATA EP,RHOP,QS,DP,DS,KF,CEOCO,TEMP,RS,NF,CO/0.63,0.67E6,0.25,     CRA03170
     / 1.3957E-6,1.12E-8,0.1873,0.213,8.0,0.078,3.125,1000.0/            CRA03180
                                                                         CRA03190
*     PH 7,TEMP 8 C; OXYGEN PURGED = 0.00, C MASS = 28.6                 CRA03200
*     EXPERIMENTAL TIME AND REDUCED CONCENTRATION                        CRA03210
                                                                         CRA03220
      DATA TEXP / 0.0,0.16,0.50,1.083,1.583,2.083,3.083,5.083,7.083,     CRA03230
     /          9.583,12.083,24.083,36.083,48.083,72.083/                CRA03240
      DATA CEXP / 1.0,0.751,0.595,0.465,0.373,0.355,0.328,0.296,         CRA03250
     /          0.289,0.281,0.271,0.249,0.237,0.226,0.213/               CRA03260
                                                                         CRA03270
      END                                                                CRA03280
*************************************************************************CRA03290
                                                                         CRA03300
```

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```
      SUBROUTINE INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,     CRA03310
     /                   Q,QMID, QAVG,CBAR )                             CRA03320
*                                                                        CRA03330
* THIS SUBROUTINE CALCULATES THE INITIAL VALUES OF THE REQUIRED          CRA03340
* PARAMETERS                                                            CRA03350
*                                                                        CRA03360
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                               CRA03370
      DOUBLE PRECISION KF,NF,LAMBDA                                      CRA03380
      PARAMETER ( NN = 100 )                                             CRA03390
      DIMENSION Q(NN,0:1),QMID(NN), QAVG(0:1),CBAR(0:1)                  CRA03400
C     DIMENSION Q(NN,0),QMID(NN), QAVG(MM),CBAR(MM)                      CRA03410
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                            CRA03420
      COMMON /INDATA2/RHOP,CO,TEMP                                       CRA03430
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                  CRA03440
                                                                         CRA03450
      PSI = EP/RHOP                                                      CRA03460
      CEQUIL = CO*CEOCO                                                  CRA03470
      UPTAKE  =  1.0D0 - CEOCO                                           CRA03480
      DTAU    = 100.0D0/DBLE( M )                                        CRA03490
      DR      = 1.0D0/DBLE( N-1 )                                        CRA03500
                                                                         CRA03510
      LAMBDA   = KF*CO**(1.0/NF)/( 1.0D0 + KF*CO**(1.0/NF) )             CRA03520
      QINFQO = KF*(CEQUIL)**(1.0D0/NF)/LAMBDA/                           CRA03530
     &          ( 1.0D0+KF*(CEQUIL)**(1.0D0/NF) )                        CRA03540
      ALPHA   =  (1.0D0 - CEOCO)/QINFQO                                  CRA03550
                                                                         CRA03560
*** INITIALIZATION : AT TAU = 0                                          CRA03570
      DO 10 I =  1,N                                                     CRA03580
      Q(I,0)   =  0.0D0                                                  CRA03590
      QMID(I)  =  EPSI2*DBLE(I)                                          CRA03600
  10  CONTINUE                                                           CRA03610
      QAVG(0)  =  0.0D0                                                  CRA03620
      CBAR(0)  =  1.0D0                                                  CRA03630
                                                                         CRA03640
      WRITE(7,*)   NF,KF,CO,CEOCO                                        CRA03650
      PRINT20, NF,KF,CO,CEOCO                                            CRA03660
   20 FORMAT(7X,' ADSORPTION OF PHENOL ON GAC ',                         CRA03670
     /     /,7X, 30('-'), /,                                           CRA03680
     /     /,3X,'LANGMUIR FREUNDLICH ISOTHERM CONSTANT      = ',F9.3.  CRA03690
     /     /,3X,'LANGMUIR FREUNDLICH EQUILIBRIUM PARAMETER  = ',F9.3.  CRA03700
     /     /,3X,'INITIAL CONCENTRATION       = ',F9.3,                  CRA03710
     /     /,3X,'CBAR AT INFINITY            = ',F9.3)                  CRA03720
                                                                         CRA03730
      PRINT30, LAMBDA, UPTAKE, QINFQO,ALPHA                              CRA03740
   30 FORMAT( 1X, ' LAMBDA                    = ',F6.3,                  CRA03750
     /      /,1X, ' UPTAKE                    = ',F6.3,                  CRA03760
     /      /,1X, ' QBAR AT INFINITY(QINFQO) = ',F6.3,                  CRA03770
     /      /,1X, ' ALPHA                     = ',F6.3 )                 CRA03780
                                                                         CRA03790
                                                                         CRA03800
      RETURN                                                             CRA03810
      END                                                                CRA03820
                                                                         CRA03830
*************************************************************************CRA03840
      SUBROUTINE OUTPUT(N,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)   CRA03850
```

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```
                                                                      CRA03860
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                           CRA03870
      DIMENSION SQTAU(N).CTAU(N),DSCAL(N),UPCAL(N),UPEXP(N)           CRA03880
                                                                      CRA03890
      PRINT5                                                          CRA03900
 5    FORMAT(/,4X,'I',11X,'SQTAU(I)',9X,'UPEXP(I)',9X,'UPEXP(I)',/,   CRA03910
     /        65('=') )                                              CRA03920
      DO 10 I = 1, N                                                  CRA03930
 10   PRINT20,I, SQTAU(I), UPEXP(I), UPCAL(I)                        CRA03940
 20   FORMAT( 3X,I2, 5X,F12.6, 5X, F12.6,5X,F12.6,/ )                 CRA03950
                                                                      CRA03960
      PRINT30                                                         CRA03970
 30   FORMAT(/,4X,'I',11X,'CTAU(I)',9X,'DSCAL(I)',/,                  CRA03980
     /        45('=') )                                              CRA03990
      DO 40 I = 1, N                                                  CRA04000
 40   PRINT50,I, CTAU(I), DSCAL(I)                                    CRA04010
 50   FORMAT( 3X,I2, 5X,F12.6, 5X, E12.6,/ )                          CRA04020
      PRINT*, 'BEST FIT DS VALUE IS =', DSFIT                         CRA04030
      PRINT*, 'RMS VALUE IS  =', RMS2                                 CRA04040
                                                                      CRA04050
      RETURN                                                          CRA04060
      END                                                             CRA04070
                                                                      CRA04080
```

Appendix A2

Optimization Program to Calculate Parameters for Batch Diffusion Systems.

FILE: A2 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
**********************************************************************  A2 00010
*                        APPENDIX A2                                 *  A2 00020
* OPTIMIZATION PROGRAM TO CALCULATE PARAMETERS FOR DIFFUSION          *  A2 00030
*                                                                    *  A2 00040
* THIS PROGRAM CALCULATES X = DS/DP FROM WHICH DS IS  OBTAINED       *  A2 00050
*                                                                    *  A2 00060
**********************************************************************  A2 00070
C-----------------------------------------------------------------------  A2 00080
C IMSL Name:  BCPOL/DBCPOL (Single/Double precision version)             A2 00090
C                                                                        A2 00100
C Purpose:    Minimize a function of N variables subject to bounds on    A2 00110
C             the variables using a direct search complex algorithm.     A2 00120
C                                                                        A2 00130
C Usage:      CALL BCPOL (FCN, N, XGUESS, IBTYPE, XLB, XUB, FTOL,        A2 00140
C                         MAXFCN, X, FVALUE)                           A2 00150
C                                                                        A2 00160
C-----------------------------------------------------------------------  A2 00170
C                                                                        A2 00180
      INTEGER    N                                                       A2 00190
      PARAMETER  (N=1)                                                   A2 00200
C                                                                        A2 00210
      INTEGER    IBTYPE, K, MAXFCN, NOUT                                 A2 00220
      REAL       FTOL, FVALUE, X(N), XGUESS(N), XLB(N), XUB(N)           A2 00230
      EXTERNAL   BCPOL, FCN, UMACH                                       A2 00240
C                                                                        A2 00250
      DATA  XGUESS/1.2/, XLB/2.0E-5/, XUB/1.0/                           A2 00260
C                                                                        A2 00270
      FTOL   = 1.0E-5                                                    A2 00280
      IBTYPE = 0                                                         A2 00290
      MAXFCN = 300                                                       A2 00300
C                                                                        A2 00310
      CALL BCPOL (FCN, N, XGUESS, IBTYPE, XLB, XUB, FTOL, MAXFCN, X,     A2 00320
     &            FVALUE)                                                A2 00330
C                                                                        A2 00340
      CALL UMACH (2, NOUT)                                               A2 00350
      WRITE (NOUT,99)  X(1), FVALUE                                      A2 00360
   99 FORMAT ('  THE BEST ESTIMATE FOR THE MINIMUM VALUE OF THE', /,     A2 00370
     &       '  FUNCTION IS X = (', (2X,F4.2), ')', /, '  WITH ',       A2 00380
     &       'function value FVALUE = ', E12.6)                          A2 00390
C                                                                        A2 00400
      END                                                                A2 00410
                                                                         A2 00420
C External function to be minimized                                      A2 00430
                                                                         A2 00440
      SUBROUTINE FCN (N, X, F)                                           A2 00450
      INTEGER    N                                                       A2 00460
      REAL       X(N), F                                                 A2 00470
C                                                                        A2 00480
      CALL CRANK6N ( X, RMS )                                            A2 00490
      F = RMS                                                            A2 00500
      RETURN                                                             A2 00510
      END                                                                A2 00520
                                                                         A2 00530
**********************************************************************  A2 00540
*                                                                      A2 00550
```

```
      SUBROUTINE CRANK6N (X, RMS)                                          A2 00560
*                                                                          A2 00570
* LAGMUIR FREUNDLICH ISOTHERM : GENERAL PROGRAM FOR PORE AND SURFACE       A2 00580
* DIFFUSION MODEL AND SURFACE DIFFUSION MODEL WITH PROVISION MADE FOR      A2 00590
* ACCOUNTING FOR CONCENTRATION DEPENDENCE VIA DARKEN'S RELATION.           A2 00600
*                                                                          A2 00610
*                                                                          A2 00620
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                A2 00630
      DOUBLE PRECISION KF,NF,LAMBDA                                        A2 00640
      PARAMETER(N=51,M=1000,NEXP=15)                                       A2 00650
      DIMENSION Q(N,0:M),QNEW(N),QOLD(N),QAVG(0:M),QMID(N),                A2 00660
     / CBAR(0:M),TAU(0:M),A(N),B(N),C(N),D(N),                             A2 00670
     / CCAL(NEXP), TEXP(NEXP),CEXP(NEXP),ETAU(NEXP),DSCAL(NEXP),           A2 00680
     / CTAU(NEXP), SQTAU(NEXP), UPCAL(NEXP),UPEXP(NEXP)                    A2 00690
      COMMON /INEXP/TEXP,CEXP                                              A2 00700
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                              A2 00710
      COMMON /INDATA2/RHOP,CO,TEMP                                         A2 00720
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                    A2 00730
      EXTERNAL AVERAGE,THOMAS,LOAD,INTER,POLATE,INITIA,OUTPUT              A2 00740
                                                                           A2 00750
      CALL INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,             A2 00760
     /             Q,QMID, QAVG,CBAR )                                     A2 00770
                                                                           A2 00780
*** GENERAL LOOP                                                           A2 00790
                                                                           A2 00800
      DO 400 J = 0, M-1                                                    A2 00810
      ITER1 = 0                                                            A2 00820
      ITER2 = 0                                                            A2 00830
      TAU(J) = REAL(J)*DTAU                                                A2 00840
  399 CONTINUE                                                             A2 00850
      DO 20  I = 1, N                                                      A2 00860
   20 QOLD(I)  = Q(I,J)                                                    A2 00870
      IF ( ITER1 .EQ. 0) THEN                                              A2 00880
                                                                           A2 00890
      QAVG(J+1) = QAVG(J) + EPSI1                                          A2 00900
      CHECK = EPSI1                                                        A2 00910
      ELSE                                                                 A2 00920
                                                                           A2 00930
      CALL AVERAGE ( N,QNEW,DR,QAV )                                       A2 00940
      CHECK = ABS ( QAVG(J+1) - QAV )                                      A2 00950
      QAVG(J+1) = QAV                                                      A2 00960
                                                                           A2 00970
      ENDIF                                                                A2 00980
                                                                           A2 00990
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                                 A2 01000
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/                  A2 01010
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )                  A2 01020
                                                                           A2 01030
      QNNEW     = Q(N,J+1)                                                 A2 01040
                                                                           A2 01050
      IF ( ITER2 .EQ. 0 ) THEN                                             A2 01060
                                                                           A2 01070
      DO 30 I = 1 , N                                                      A2 01080
   30 QMID(I) = QMID(I) + EPSI2*(I)                                        A2 01090
      ELSE                                                                 A2 01100
```

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FILE: A2        FORTRAN  A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS. DHAHRAN

      DO 40 I = 1 , N                                                    A2 01110
 40   QMID(I) = ( Q(I,J) + Q(I,J+1) )/ 2.0D0                            A2 01120
      ENDIF                                                              A2 01130
                                                                         A2 01140
      ITER1 = ITER1 + 1                                                  A2 01150
      ITER2 = ITER2 + 1                                                  A2 01160
                                                                         A2 01170
      CALL LOAD ( X,N,DTAU,DR,LAMBDA,QOLD,QMID,QNNEW,A,B,C,D )           A2 01180
      CALL THOMAS ( N,A,B,C,D,QNEW )                                     A2 01190
                                                                         A2 01200
      DO 50 I = 1, N                                                     A2 01210
      Q(I,J+1) = QNEW(I)                                                 A2 01220
 50   CONTINUE                                                           A2 01230
                                                                         A2 01240
      IF  ( (CHECK .GT. ERROR ) .AND. ( ITER1 .LT. 50) ) GOTO 399        A2 01250
                                                                         A2 01260
 400  CONTINUE                                                           A2 01270
      CALL POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,              A2 01280
     /             CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)               A2 01290
                                                                         A2 01300
C     CALL INTER(M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,CEXP,CTAU,DSCAL)        A2 01310
      CALL OUTPUT(NEXP,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)      A2 01320
                                                                         A2 01330
                                                                         A2 01340
      END                                                                A2 01350
                                                                         A2 01360
*************************************************************************A2 01370
                                                                         A2 01380
      SUBROUTINE THOMAS ( N,A,B,C,D,X)                                   A2 01390
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                              A2 01400
**********************************************************             A2 01410
* THOMAS ALGORYTHM FOR SOLVING A TRIDIAGONAL MATRIX        *            A2 01420
**********************************************************             A2 01430
                                                                         A2 01440
      PARAMETER( M =100)                                                 A2 01450
      DIMENSION A(N),B(N),C(N),D(N),X(N),GAM(M),BET(M)                   A2 01460
                                                                         A2 01470
      BET(1) = B(1)                                                      A2 01480
      GAM(1) = D(1)/B(1)                                                 A2 01490
      DO 320 I = 2, N                                                    A2 01500
      BET(I) = B(I) -  A(I)*C(I-1)/BET(I-1)                              A2 01510
      GAM(I) = ( D(I) - A(I)*GAM(I-1) )/BET(I)                           A2 01520
 320  CONTINUE                                                           A2 01530
      X(N) = GAM(N)                                                      A2 01540
      DO 330 I = N -1,1,-1                                               A2 01550
      X(I) = GAM(I) - C(I)*X(I+1)/BET(I)                                 A2 01560
 330  CONTINUE                                                           A2 01570
                                                                         A2 01580
      RETURN                                                             A2 01590
      END                                                                A2 01600
                                                                         A2 01610
*************************************************************************A2 01620
                                                                         A2 01630
      SUBROUTINE AVERAGE( N,Q,DF,QAVG)                                   A2 01640
* INTEGRATION VIA SIMPSON'S COMPOSITE RULE                              A2 01650
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FILE: A2        FORTRAN  A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

* RETURNS THE AVERAGE VALUE OF THE SOLID PHASE CONCENTRATION            A2 01660
                                                                        A2 01670
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               A2 01680
      DIMENSION Q(N)                                                    A2 01690
                                                                        A2 01700
      XI0 = Q(1)*0.0*0.0 +  Q(N)*1.0*1.0                                A2 01710
      XI1 = 0.0D0                                                       A2 01720
      XI2 = 0.0D0                                                       A2 01730
      DO 350  I = 2, N-1                                                A2 01740
      IF ( MOD(I,2) .EQ. 0 ) THEN                                       A2 01750
      XI2 = XI2 + Q(I)*( (DR*REAL(I-1))**2 )                            A2 01760
      ELSE                                                              A2 01770
      XI1 = XI1 + Q(I)*( (DR*REAL(I-1))**2 )                            A2 01780
      ENDIF                                                             A2 01790
  350 CONTINUE                                                          A2 01800
      XI = (DR/3.0D0)*( XI0  + 4.0D0*XI2 + 2.0D0*XI1 )                  A2 01810
      QAVG = 3.0D0*XI                                                   A2 01820
                                                                        A2 01830
      RETURN                                                            A2 01840
      END                                                               A2 01850
                                                                        A2 01860
*****************************************************************     A2 01870
      SUBROUTINE LOAD ( X,N,DTAU,DR,LAMBDA,QOLD,QMID,QNNEW,A,B,C,D )    A2 01880
*                                                                       A2 01890
*THIS PROGRAM CALCULATES THE VALUES OF A,B,C AND D REQUIRED IN THOMAS   A2 01900
* ALGORYTHM.                                                           A2 01910
*                                                                       A2 01920
      IMPLICIT DOUBLE PRECISION ( A-H,O-Z)                              A2 01930
      DOUBLE PRECISION KF,NF,LAMBDA                                     A2 01940
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           A2 01950
      COMMON /INDATA2/RHOP,CO,TEMP                                      A2 01960
      PARAMETER ( M =100 )                                              A2 01970
      DIMENSION QOLD(N),QMID(N),A(M),B(M),C(M),D(M),P(M),F(M),OMEGA(M), A2 01980
     /          PO(M)                                                  A2 01990
                                                                        A2 02000
      PHI = DTAU/DR**2                                                  A2 02010
      NM1 = N-1                                                         A2 02020
      PSI = EP/RHOP                                                     A2 02030
                                                                        A2 02040
      DO 10 I = 1, N                                                    A2 02050
      IF ( QMID(I) .GT. 1.0 ) THEN                                      A2 02060
      QMID(I) = 0.999990D0                                              A2 02070
      ELSE                                                              A2 02080
      ENDIF                                                             A2 02090
      QL = LAMBDA*QMID(I)                                               A2 02100
      IF ( ( QMID(I) .EQ. 0.0).OR.(QL .LT. 1.0E-75) ) THEN              A2 02110
      DCDQ = (NF/(KF**NF)/QS)                                           A2 02120
      ELSE                                                              A2 02130
      DCDQ = (NF/(KF**NF)/QS)*(QL**(NF-1.0))/((1.0-QL)**(NF+1.0))       A2 02140
      ENDIF                                                             A2 02150
                                                                        A2 02160
** FOR HSDM CONSTANT DS MODEL :                                        A2 02170
C     PO(I)  =  X                                                       A2 02180
** FOR HSDM CONCENTRATION DEPEDENT DS MODEL :                          A2 02190
C     PO(I)  = PSI*DCDQ + X                                             A2 02200
```

```
** FOR PSD CONSTANT DS MODEL :                                          A2 02210
      PO(I)  =  X*NF/(1.0 - QL)                                        A2 02220
** FOR PSD CONCENTRATION DEPEDENT DS MODEL :                           A2 02230
C      PO(I)  = PSI*DCDQ + X*NF/(1.0 - QL)                             A2 02240
                                                                       A2 02250
   10 CONTINUE                                                         A2 02260
                                                                       A2 02270
      DO 20 I = 2, NM1                                                 A2 02280
      F(I) =(PHI/4.0D0)*(2.0D0*PO(I)/DBLE(I-1)+(PO(I+1)-PO(I-1))/2.0D0 )A2 02290
   20 CONTINUE                                                         A2 02300
*                                                                      A2 02310
* BOUNDARY NODE 1                                                      A2 02320
*                                                                      A2 02330
      A(1) = 0.0                                                       A2 02340
      B(1) = 1.0D0 + 3.0D0*PHI*PO(1)                                   A2 02350
      C(1) = - 3.0D0*PHI*PO(1)                                         A2 02360
      D(1) =( 2.0D0 - B(1))*QOLD(1) - C(1)*QOLD(2)                     A2 02370
*                                                                      A2 02380
* INTERIOR NODES 2 TO NM1                                              A2 02390
*                                                                      A2 02400
      DO 30 I = 2, NM1                                                 A2 02410
      A(I) = -PHI*PO(I)/2.0D0 + F(I)                                   A2 02420
      B(I) = 1.0D0 + PHI*PO(I)                                         A2 02430
      C(I) = -PHI*PO(I)/2.0D0 - F(I)                                   A2 02440
      D(I) = -A(I)*QOLD(I-1)+(2.0-B(I))*QOLD(I)- C(I)*QOLD(I+1)        A2 02450
  30  CONTINUE                                                         A2 02460
*                                                                      A2 02470
* BOUNDARY NODE N                                                      A2 02480
*                                                                      A2 02490
      A(N) = 0.0                                                       A2 02500
      B(N) = 1.0D0                                                     A2 02510
      C(N) = 0.0                                                       A2 02520
      D(N) = QNNEW                                                     A2 02530
                                                                       A2 02540
      RETURN                                                           A2 02550
      END                                                              A2 02560
                                                                       A2 02570
*****************************************************************      A2 02580
                                                                       A2 02590
      SUBROUTINE INTER ( M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,              A2 02600
     /                   CEXP,CTAU,DSCAL)                              A2 02610
*****************************************************************      A2 02620
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY.                A2 02630
* THE DIFFUSIVITY COEFFICIENT IS CALCULATED FROM THE        *          A2 02640
* RELATION : DSCAL = TAU*RS*RS/TIME                         *          A2 02650
*                                                           *          A2 02660
*****************************************************************      A2 02670
*                                                                      A2 02680
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                            A2 02690
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),CTAU(NEXP),       A2 02700
     /          DSCAL(NEXP)                                           A2 02710
                                                                       A2 02720
      DO 100 IEXP = 2, NEXP                                            A2 02730
*                                                                      A2 02740
* SCAN THROUGH THE DATA                                                A2 02750
```

```
*                                                                       A2 02760
      ISCAN = 0                                                         A2 02770
   10 CONTINUE                                                          A2 02780
      ISCAN = ISCAN + 1                                                 A2 02790
      IF ( CEXP(IEXP) .LT. CBAR(ISCAN) ) GOTO 10                        A2 02800
*                                                                       A2 02810
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                         A2 02820
*                                                                       A2 02830
      CTAU(IEXP) = ( TAU(ISCAN) - TAU(ISCAN+1) )                        A2 02840
     /             *( ( CEXP(IEXP) - CBAR(ISCAN+1))/                   A2 02850
     /             (CBAR(ISCAN)-CBAR(ISCAN+1))) + TAU(ISCAN+1)         A2 02860
      DPCAL = CTAU(IEXP)*RS*RS/( TEXP(IEXP)*60.0**2)                    A2 02870
      DSCAL(IEXP) = DPCAL*X                                             A2 02880
                                                                        A2 02890
  100 CONTINUE                                                          A2 02900
                                                                        A2 02910
      RETURN                                                            A2 02920
      END                                                               A2 02930
                                                                        A2 02940
*************************************************************************A2 02950
                                                                        A2 02960
      SUBROUTINE POLATE (M,NEXP,RS,CEOCO,X,CBAR.TAU,TEXP,DP,CEXP,       A2 02970
     /                   CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)         A2 02980
                                                                        A2 02990
*************************************************************          A2 03000
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY AND              A2 03010
* CALCULATES THE ROOT MEAN SQUARE OF THE DEVIATIONS OF                  A2 03020
* PREDICTED CONCENTRATION VALUES FROM EXPERIMENTAL VALUES               A2 03030
*************************************************************          A2 03040
*                                                                       A2 03050
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A2 03060
      PARAMETER ( N = 20 )                                              A2 03070
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),SQTAU(N),          A2 03080
     /          ETAU(N),CCAL(N),UPCAL(N),UPEXP(N)                      A2 03090
                                                                        A2 03100
      DO 10 I = 1, NEXP                                                 A2 03110
      ETAU(I) = DP*TEXP(I)*60.0**2/RS**2                                A2 03120
  10  CONTINUE                                                          A2 03130
                                                                        A2 03140
      RMS = 0.0                                                         A2 03150
      RMS2 = 0.0                                                        A2 03160
                                                                        A2 03170
      DO 100 I = 2, NEXP                                                A2 03180
      ISCAN = 0                                                         A2 03190
   20 CONTINUE                                                          A2 03200
      ISCAN = ISCAN + 1                                                 A2 03210
      IF ( ETAU(I) .GT. TAU(ISCAN) ) GOTO 20                            A2 03220
*                                                                       A2 03230
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                         A2 03240
*                                                                       A2 03250
      CCAL(I)=(CBAR(ISCAN)-CBAR(ISCAN+1))*((ETAU(IEXP)-TAU(ISCAN))/     A2 03260
     /        (TAU(ISCAN) - TAU(ISCAN+1))) + CBAR(ISCAN+1)              A2 03270
                                                                        A2 03280
      IF ( I .NE. 1 ) THEN                                              A2 03290
      RMS2 = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS2                    A2 03300
```

```
      ELSE                                                              A2 03310
      ENDIF                                                             A2 03320
      RMS = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS                      A2 03330
                                                                        A2 03340
      SQTAU(I) = SQRT( ETAU(I) )                                        A2 03350
      UPCAL(I) = ABS(1.0 - CCAL(I) )/( 1.0 - CEOCO )                    A2 03360
      UPEXP(I) = ABS(1.0 - CEXP(I) )/( 1.0 - CEOCO )                    A2 03370
                                                                        A2 03380
  100 CONTINUE                                                          A2 03390
                                                                        A2 03400
      RMS = 100.0*SQRT(RMS/REAL(NEXP))                                  A2 03410
      RMS2 = 100.0*SQRT(RMS2/REAL(NEXP-1))                              A2 03420
      DSFIT = DP*X                                                      A2 03430
                                                                        A2 03440
      RETURN                                                            A2 03450
      END                                                               A2 03460
                                                                        A2 03470
*******************************************************************************A2 03480
      BLOCK DATA                                                        A2 03490
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                              A2 03500
      DOUBLE PRECISION KF,NF                                            A2 03510
      PARAMETER ( N =15 )                                               A2 03520
      DIMENSION TEXP(N), CEXP(N)                                        A2 03530
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           A2 03540
      COMMON /INDATA2/RHOP,CO,TEMP                                      A2 03550
      COMMON /INEXP/TEXP,CEXP                                           A2 03560
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                 A2 03570
                                                                        A2 03580
      DATA EPSI1, EPSI2, ERROR / 1.0D-8,1.0D-9,1.0D-13/                 A2 03590
      DATA EP,RHOP,QS,DP,KF,CEOCO,TEMP,RS,NF,CO/0.63,0.67E6,0.25.       A2 03600
     / 1.3957E-6,0.1873,0.213,8.0,0.078,3.125,1000.0/                   A2 03610
                                                                        A2 03620
*     PH 7,TEMP 8 C; OXYGEN PURGED = 0.00, C MASS = 28.6                A2 03630
*     EXPERIMENTAL TIME AND REDUCED CONCENTRATION                       A2 03640
                                                                        A2 03650
      DATA TEXP / 0.0,0.16,0.50,1.083,1.583,2.083,3.083,5.083,7.083,    A2 03660
     /           9.583,12.083,24.083,36.083,48.083,72.083/              A2 03670
      DATA CEXP / 1.0,0.751,0.595,0.465,0.373,0.355,0.328,0.296,        A2 03680
     /           0.289,0.281,0.271,0.249,0.237,0.226,0.213/             A2 03690
                                                                        A2 03700
      END                                                               A2 03710
*******************************************************************************A2 03720
                                                                        A2 03730
      SUBROUTINE INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,    A2 03740
     /                   Q,QMID, QAVG,CBAR )                            A2 03750
*                                                                       A2 03760
* THIS SUBROUTINE CALCULATES THE INITIAL VALUES OF THE REQUIRED         A2 03770
* PARAMETERS                                                            A2 03780
*                                                                       A2 03790
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                              A2 03800
      DOUBLE PRECISION KF,NF,LAMBDA                                     A2 03810
      PARAMETER ( NN = 100 )                                            A2 03820
      DIMENSION Q(NN,0:1),QMID(NN), QAVG(0:1),CBAR(0:1)                 A2 03830
C     DIMENSION Q(NN,0),QMID(NN), QAVG(MM),CBAR(MM)                     A2 03840
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           A2 03850
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      COMMON /INDATA2/RHOP,CO,TEMP -                                    A2 03860
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                 A2 03870
                                                                        A2 03880
      PSI = EP/RHOP                                                     A2 03890
      CEQUIL = CO*CEOCO                                                 A2 03900
      UPTAKE  =  1.0D0 - CEOCO                                          A2 03910
      DTAU    = 100.0D0/DBLE( M )                                       A2 03920
      DR      = 1.0D0/DBLE( N-1 )                                       A2 03930
                                                                        A2 03940
      LAMBDA   = KF*CO**(1.0/NF)/( 1.0D0 + KF*CO**(1.0/NF) )            A2 03950
      QINFQO = KF*(CEQUIL)**(1.0D0/NF)/LAMBDA/                          A2 03960
     &          ( 1.0D0+KF*(CEQUIL)**(1.0D0/NF) )                       A2 03970
      ALPHA   =  (1.0D0 - CEOCO)/QINFQO                                 A2 03980
                                                                        A2 03990
*** INITIALIZATION : AT TAU = 0                                         A2 04000
      DO 10 I =  1,N                                                    A2 04010
      Q(I,0)   =  0.0D0                                                 A2 04020
      QMID(I)  =  EPSI2*DBLE(I)                                         A2 04030
  10  CONTINUE                                                          A2 04040
      QAVG(0)  =  0.0D0                                                 A2 04050
      CBAR(0)  =  1.0D0                                                 A2 04060
                                                                        A2 04070
      WRITE(7,*)   NF,KF,CO,CEOCO                                       A2 04080
      PRINT20, NF,KF,CO,CEOCO                                           A2 04090
   20 FORMAT(7X,' ADSORPTION OF PHENOL ON GAC ',                        A2 04100
     /     /,7X, 30('-'), /,                                          A2 04110
     /     /,3X,'LANGMUIR FREUNDLICH ISOTHERM CONSTANT      = ',F9.3,  A2 04120
     /     /,3X,'LANGMUIR FREUNDLICH EQUILIBRIUM PARAMETER  = ',F9.3,  A2 04130
     /     /,3X,'INITIAL CONCENTRATION       = ',F9.3,                 A2 04140
     /     /,3X,'CBAR AT INFINITY            = ',F9.3)                 A2 04150
                                                                        A2 04160
      PRINT30, LAMBDA, UPTAKE, QINFQO,ALPHA                             A2 04170
   30 FORMAT( 1X, ' LAMBDA                    = ',F6.3,                 A2 04180
     /      /,1X, ' UPTAKE                    = ',F6.3,                 A2 04190
     /      /,1X, ' QBAR AT INFINITY(QINFQO) = ',F6.3,                 A2 04200
     /      /,1X, ' ALPHA                     = ',F6.3 )                A2 04210
                                                                        A2 04220
                                                                        A2 04230
      RETURN                                                            A2 04240
      END                                                               A2 04250
                                                                        A2 04260
*************************(*************************************************A2 04270
      SUBROUTINE OUTPUT(N,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)  A2 04280
                                                                        A2 04290
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A2 04300
      DIMENSION SQTAU(N),CTAU(N),DSCAL(N),UPCAL(N),UPEXP(N)             A2 04310
                                                                        A2 04320
      PRINT5                                                            A2 04330
 5    FORMAT(/,4X,'I',11X,'SQTAU(I)',9X,'UPEXP(I)',9X,'UPEXP(I)',/,     A2 04340
     /        65('=') )                                                A2 04350
      DO 10 I = 1, N                                                    A2 04360
 10   PRINT20,I, SQTAU(I), UPEXP(I), UPCAL(I)                           A2 04370
 20   FORMAT( 3X,I2, 5X,F12.6, 5X, F12.6,5X,F12.6,/ )                   A2 04380
                                                                        A2 04390
      PRINT30                                                           A2 04400
```

```
 30   FORMAT(/,4X,'I',11X,'CTAU(I)',9X,'DSCAL(I)'./,                    A2 04410
     /        45('=') )                                                 A2 04420
      DO 40 I = 1, N                                                    A2 04430
 40   PRINT50,I, CTAU(I), DSCAL(I)                                      A2 04440
 50   FORMAT( 3X,I2, 5X,F12.6, 5X, E12.6,/ )                            A2 04450
      PRINT*, 'BEST FIT DS VALUE IS =', DSFIT                           A2 04460
      PRINT*, 'RMS VALUE IS  =', RMS2                                   A2 04470
                                                                        A2 04480
      RETURN                                                            A2 04490
      END                                                               A2 04500
```

Appendix A3

Program for Pore and Surface Diffusion with Reaction in Batch Systems.

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```
************************************************************************     CRA00010
*                          APPENDIX A3                                 *     CRA00020
*   PROGRAM FOR PORE & SURFACE DIFFUSION WITH REACTIOI. IN BATCH       *     CRA00030
*   SYSTEMS                                                            *     CRA00040
*                                                                      *     CRA00050
************************************************************************     CRA00060
      PROGRAM CRANK8N                                                         CRA00070
*                                                                             CRA00080
* LAGMUIR FREUNDLICH ISOTHERM : PORE AND SURFACE DIFFUSION MODEL              CRA00090
* WITH REACTION                                                              CRA00100
*                                                                             CRA00110
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                   CRA00120
      DOUBLE PRECISION KF,NF,LAMBDA                                           CRA00130
      PARAMETER(N=61,M=2000,NEXP=20 )                                         CRA00140
      DIMENSION Q(N,0:M),QNEW(N),QOLD(N),QAVG(0:M),QMID(N),                   CRA00150
     / CBAR(0:M),TAU(0:M),A(N),B(N),C(N),D(N),                                CRA00160
     / CCAL(NEXP), TEXP(NEXP), CEXP(NEXP), ETAU(NEXP), DSCAL(NEXP),           CRA00170
     / CTAU(NEXP),SQTAU(NEXP),UPCAL(NEXP),UPEXP(NEXP), RTERM(NEXP)            CRA00180
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                                 CRA00190
      COMMON /INDATA2/RHOP,CO,TEMP                                            CRA00200
      COMMON /INEXP/TEXP,CEXP                                                 CRA00210
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                       CRA00220
      COMMON /RRX/ CONST, ORDER1, ORDER2, RCONC                               CRA00230
                                                                              CRA00240
      EXTERNAL AVERAGE, THOMAS, LOAD, INTER, POLATE,RXN                       CRA00250
                                                                              CRA00260
      CALL INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,                CRA00270
     /             Q,QMID, QAVG,CBAR )                                        CRA00280
                                                                              CRA00290
      DS = 0.98E-8                                                            CRA00300
C     DP = 1.3957E-6                                                          CRA00310
                                                                              CRA00320
      X  = DP/DS                                                              CRA00330
                                                                              CRA00340
*** GENERAL LOOP                                                             CRA00350
                                                                              CRA00360
      DO 400 J = 0, M-1                                                       CRA00370
                                                                              CRA00380
      ISUME1 = 0                                                              CRA00390
      ISUME2 = 0                                                              CRA00400
      TAU(J) = REAL(J)*DTAU                                                   CRA00410
  399 CONTINUE                                                                CRA00420
                                                                              CRA00430
      DO 20  I = 1, N                                                         CRA00440
   20 QOLD(I)  = Q(I,J)                                                       CRA00450
                                                                              CRA00460
      IF ( ISUME1 .EQ. 0) THEN                                                CRA00470
                                                                              CRA00480
      QAVG(J+1) = QAVG(J) + EPSI1                                             CRA00490
      CHECK = EPSI1                                                           CRA00500
      ELSE                                                                    CRA00510
                                                                              CRA00520
      CALL AVERAGE ( N,QNEW,DR,QAV )                                          CRA00530
      CHECK = ABS ( QAVG(J+1) - QAV )                                         CRA00540
      QAVG(J+1) = QAV                                                         CRA00550
```

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```
                                                                      CRA00560
      ENDIF                                                           CRA00570
                                                                      CRA00580
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                            CRA00590
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/             CRA00600
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )            CRA00610
                                                                      CRA00620
      QNNEW     = Q(N,J+1)                                            CRA00630
                                                                      CRA00640
      IF ( ISUME2 .EQ. 0 ) THEN                                       CRA00650
                                                                      CRA00660
      DO 30 I = 1 , N                                                 CRA00670
 30   QMID(I) = QMID(I) + EPSI2*(I)                                   CRA00680
      ELSE                                                            CRA00690
      DO 40 I = 1 , N                                                 CRA00700
 40   QMID(I) = ( Q(I,J) + Q(I,J+1) )/ 2.0D0                          CRA00710
      ENDIF                                                           CRA00720
                                                                      CRA00730
      ISUME1 = ISUME1 + 1                                             CRA00740
      ISUME2 = ISUME2 + 1                                             CRA00750
                                                                      CRA00760
       DO 45 I = 1 , N                                                CRA00770
 45    RTERM(I) = 0.0                                                 CRA00780
                                                                      CRA00790
** CALL SUBROUTINE LOAD TO SET UP THE TRIDIAGONAL MATRIX              CRA00800
                                                                      CRA00810
      CALL LOAD (X,RTERM,N.DTAU,DR,QOLD,QMID,QNNEW,A,B,C,D,DS,LAMBDA) CRA00820
                                                                      CRA00830
      CALL THOMAS ( N,A,B,C,D,QNEW )                                  CRA00840
                                                                      CRA00850
      DO 50 I = 1, N                                                  CRA00860
      Q(I,J+1) = QNEW(I)                                              CRA00870
 50   CONTINUE                                                        CRA00880
      TAUJ = TAU(J)                                                   CRA00890
                                                                      CRA00900
      IF  ( (CHECK .GT. ERROR ) .AND. ( ISUME1 .LT. 50) ) GOTO 399    CRA00910
                                                                      CRA00920
      CALL RXN(N,TAUJ,DTAU.RS,DS,RCONC,ORDER1,ORDER2,CONST,QOLD,RTERM) CRA00930
                                                                      CRA00940
      CALL LOAD (X,RTERM,N,DTAU,DR,QOLD,QMID,QNNEW,A,B,C,D,DS,LAMBDA) CRA00950
                                                                      CRA00960
      CALL THOMAS ( N,A,B,C,D,QNEW )                                  CRA00970
                                                                      CRA00980
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                            CRA00990
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/             CRA01000
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )            CRA01010
                                                                      CRA01020
      QNNEW     = Q(N,J+1)                                            CRA01030
                                                                      CRA01040
      DO 60 I = 1, N                                                  CRA01050
      Q(I,J+1) = QNEW(I)                                              CRA01060
 60   CONTINUE                                                        CRA01070
                                                                      CRA01080
C     PRINT*, TAU(J) , CBAR(J)                                        CRA01090
      WRITE(7,*) TAU(J) , CBAR(J)                                     CRA01100
```

```
                                                                      CRA01110
  400 CONTINUE                                                        CRA01120
                                                                      CRA01130
                                                                      CRA01140
      CALL POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,           CRA01150
     /             CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)             CRA01160
                                                                      CRA01170
      CALL INTER  ( M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,                  CRA01180
     /              CEXP,CTAU,DSCAL)                                 CRA01190
                                                                      CRA01200
      CALL OUTPUT(NEXP,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)   CRA01210
                                                                      CRA01220
      END                                                             CRA01230
                                                                      CRA01240
*****************************************************************************CRA01250
                                                                      CRA01260
      SUBROUTINE THOMAS ( N,A,B,C,D,X)                                CRA01270
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                           CRA01280
*************************************************************       CRA01290
* THOMAS ALGORYTHM FOR SOLVING A TRIDIAGONAL MATRIX        *         CRA01300
*************************************************************       CRA01310
                                                                      CRA01320
      PARAMETER( M =100)                                              CRA01330
      DIMENSION A(N),B(N),C(N),D(N),X(N),GAM(M),BET(M)                CRA01340
                                                                      CRA01350
      BET(1) = B(1)                                                   CRA01360
      GAM(1) = D(1)/B(1)                                              CRA01370
      DO 320 I = 2, N                                                 CRA01380
      BET(I) = B(I) -  A(I)*C(I-1)/BET(I-1)                           CRA01390
      GAM(I) = ( D(I) - A(I)*GAM(I-1) )/BET(I)                        CRA01400
  320 CONTINUE                                                        CRA01410
      X(N) = GAM(N)                                                   CRA01420
      DO 330 I = N -1,1,-1                                            CRA01430
      IF (X(I+1) .LT. 1.0E-77 ) THEN                                  CRA01440
      X(I+1) = GAM(I)                                                 CRA01450
      ELSE                                                            CRA01460
      X(I) = GAM(I) - C(I)*X(I+1)/BET(I)                              CRA01470
      ENDIF                                                           CRA01480
  330 CONTINUE                                                        CRA01490
                                                                      CRA01500
      DO 333 I = 1,N                                                  CRA01510
  333 CONTINUE                                                        CRA01520
      RETURN                                                          CRA01530
      END                                                             CRA01540
                                                                      CRA01550
*****************************************************************************CRA01560
                                                                      CRA01570
      SUBROUTINE AVERAGE( N,Q,DR,QAVG)                                CRA01580
* INTEGRATION VIA SIMPSON'S COMPOSITE RULE                           CRA01590
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                             CRA01600
      DIMENSION Q(N)                                                  CRA01610
                                                                      CRA01620
      XI0 = Q(1)*0.0*0.0 +  Q(N)*1.0*1.0                              CRA01630
      XI1 = 0.0D0                                                     CRA01640
      XI2 = 0.0D0                                                     CRA01650
```

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```
      DO 350  I = 2, N-1                                                    CRA01660
      IF ( MOD(I,2) .EQ. 0 ) THEN                                           CRA01670
      XI2 = XI2 + Q(I)*( (DR*REAL(I-1))**2 )                                CRA01680
      ELSE                                                                  CRA01690
      XI1 = XI1 + Q(I)*( (DR*REAL(I-1))**2 )                                CRA01700
      ENDIF                                                                 CRA01710
  350 CONTINUE                                                              CRA01720
      XI = (DR/3.0D0)*( XI0  + 4.0D0*XI2 + 2.0D0*XI1 )                      CRA01730
      QAVG = 3.0D0*XI                                                       CRA01740
                                                                            CRA01750
      RETURN                                                                CRA01760
      END                                                                   CRA01770
                                                                            CRA01780
*************************************************************************CRA01790
      SUBROUTINE LOAD (X,RTERM,N,DTAU,DR,QOLD,QMID,QNNEW, A,B,C,D,DS,       CRA01800
     /                 LAMBDA )                                           CRA01810
                                                                            CRA01820
      IMPLICIT DOUBLE PRECISION ( A-H,O-Z)                                  CRA01830
      DOUBLE PRECISION KF,NF,LAMBDA                                         CRA01840
      COMMON /INDATA1/EP,QS,DP,KF,CEOC0,RS,NF                               CRA01850
      COMMON /INDATA2/RHOP,CO,TEMP                                          CRA01860
      PARAMETER ( M =100 )                                                  CRA01870
      DIMENSION QOLD(N),QMID(N),A(M),B(M),C(M),D(M),P(M),F(M),              CRA01880
     /          PO(M),RTERM(N)                                             CRA01890
                                                                            CRA01900
      PHI = DTAU/DR**2                                                      CRA01910
      NM1 = N-1                                                             CRA01920
      PSI = EP/RHOP                                                         CRA01930
                                                                            CRA01940
      DO 10 I = 1, N                                                        CRA01950
                                                                            CRA01960
      IF ( QMID(I) .GT. 1.0 ) THEN                                          CRA01970
      QMID(I) = 0.999999990D0                                               CRA01980
      ELSE                                                                  CRA01990
      ENDIF                                                                 CRA02000
      CK = 1.0 - QL                                                         CRA02010
      IF  ( ( QL .LT. 0.0 ) .OR. (CK .LT. 0.0 ) ) THEN                      CRA02020
      DCDQ = 0.0                                                            CRA02030
      ELSE                                                                  CRA02040
      QL = LAMBDA*QMID(I)                                                   CRA02050
      DCDQ =(NF/(KF**NF)/QS)*(QL**(NF-1.0))/((1.0-QL)**(NF+1.0))            CRA02060
      ENDIF                                                                 CRA02070
                                                                            CRA02080
* FOR PSD CONSTANT DS MODEL                                                CRA02090
*     PO(I)  = PSI*DCDQ*X + 1.0                                           CRA02100
* FOR PSD WITH VARIABLE DS MODEL                                           CRA02110
      PO(I)  = PSI*DCDQ*X + NF/(1.0D0 - LAMBDA*QMID(I) )                    CRA02120
* FOR HSSD WITH VARIABLE DS MODEL                                          CRA02130
*     PO(I)  =  NF/(1.0D0 - LAMBDA*QMID(I) )                              CRA02140
                                                                            CRA02150
   10 CONTINUE                                                              CRA02160
                                                                            CRA02170
      DO 20 I = 2, NM1                                                      CRA02180
      F(I) =(PHI/4.0D0)*(2.0D0*PO(I)/DBLE(I-1)+(PO(I+1)-PO(I-1))/2.0D0 )CRA02190
   20 CONTINUE                                                              CRA02200
```

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```
*                                                                       CRA02210
* BOUNDARY NODE 1                                                       CRA02220
*                                                                       CRA02230
      A(1) = 0.0                                                        CRA02240
      B(1) = 1.0D0 + 3.0D0*PHI*PO(1)                                    CRA02250
      C(1) = - 3.0D0*PHI*PO(1)                                          CRA02260
      D(1) =( 2.0D0 - B(1))*QOLD(1) - C(1)*QOLD(2)-RTERM(1)             CRA02270
*                                                                       CRA02280
* INTERIOR NODES 2 TO NM1                                               CRA02290
*                                                                       CRA02300
      DO 30 I = 2, NM1                                                  CRA02310
      A(I) = -PHI*PO(I)/2.0D0 + F(I)                                    CRA02320
      B(I) = 1.0D0 + PHI*PO(I)                                          CRA02330
      C(I) = -PHI*PO(I)/2.0D0 - F(I)                                    CRA02340
      D(I) =-A(I)*QOLD(I-1)+(2.0-B(I))*QOLD(I)-C(I)*QOLD(I+1)-RTERM(I)  CRA02350
  30  CONTINUE                                                          CRA02360
*                                                                       CRA02370
* BOUNDARY NODE N                                                       CRA02380
*                                                                       CRA02390
      A(N) = 0.0                                                        CRA02400
      B(N) = 1.0D0                                                      CRA02410
      C(N) = 0.0                                                        CRA02420
      D(N) = QNNEW - RTERM(N)                                           CRA02430
                                                                        CRA02440
      RETURN                                                            CRA02450
      END                                                               CRA02460
*************************************************************************CRA02470
      SUBROUTINE RXN (N,TAUJ, DTAU, RS,DS,RCONC,ORDER1,ORDER2,          CRA02480
     /                CONST,QOLD,RTERM)                                 CRA02490
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             CRA02500
      DIMENSION QOLD(N),RTERM(N)                                        CRA02510
      TAUJO = 0.0                                                       CRA02520
                                                                        CRA02530
      SIGMA = RCONC*((RS**2/DS)**ORDER1)                                CRA02540
      T2 = TAUJ + DTAU/2.0                                              CRA02550
      TM =  (T2**ORDER1)*SIGMA                                          CRA02560
                                                                        CRA02570
      DO  20 I = 1, N                                                   CRA02580
      IF ( QOLD(I) .LT. 0.0 ) THEN                                      CRA02590
      RTERM(I) = DTAU*CONST*TM                                          CRA02600
      ELSE                                                              CRA02610
      RTERM(I) = DTAU*CONST*TM*(QOLD(I)**ORDER2)                        CRA02620
      ENDIF                                                             CRA02630
   20 CONTINUE                                                          CRA02640
                                                                        CRA02650
      RETURN                                                            CRA02660
      END                                                               CRA02670
                                                                        CRA02680
*************************************************************************CRA02690
                                                                        CRA02700
      SUBROUTINE INTER ( M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,               CRA02710
     /                   CEXP,CTAU,DSCAL)                               CRA02720
**********************************************************            CRA02730
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY.                 CRA02740
* THE DIFFUSIVITY COEFFICIENT IS CALCULATED FROM THE        *           CRA02750
```

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```
* RELATION : DSCAL = TAU*RS*RS/TIME                                    *          CRA02760
*                                                                      *          CRA02770
************************************************************************          CRA02780
*                                                                               CRA02790
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                     CRA02800
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),CTAU(NEXP).                CRA02810
     /          DSCAL(NEXP)                                                    CRA02820
                                                                                CRA02830
      DO 100 IEXP = 2, NEXP                                                     CRA02840
*                                                                               CRA02850
* SCAN THROUGH THE DATA                                                        CRA02860
*                                                                               CRA02870
      ISCAN = 0                                                                 CRA02880
   10 CONTINUE                                                                  CRA02890
      ISCAN = ISCAN + 1                                                         CRA02900
      IF ( CEXP(IEXP) .LT. CBAR(ISCAN) ) GOTO 10                                CRA02910
*                                                                               CRA02920
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                                CRA02930
*                                                                               CRA02940
      CTAU(IEXP) = ( TAU(ISCAN) - TAU(ISCAN+1) )                                CRA02950
     /             *( ( CEXP(IEXP) - CBAR(ISCAN+1))/                          CRA02960
     /             (CBAR(ISCAN)-CBAR(ISCAN+1))) + TAU(ISCAN+1)                CRA02970
      DPCAL = CTAU(IEXP)*RS*RS/( TEXP(IEXP)*60.0**2)                            CRA02980
      DSCAL(IEXP) = DPCAL*X                                                     CRA02990
                                                                                CRA03000
  100 CONTINUE                                                                  CRA03010
                                                                                CRA03020
      RETURN                                                                    CRA03030
      END                                                                       CRA03040
                                                                                CRA03050
************************************************************************************CRA03060
                                                                                CRA03070
      SUBROUTINE POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,               CRA03080
     /                   CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)                 CRA03090
                                                                                CRA03100
************************************************************                    CRA03110
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY AND                      CRA03120
* CALCULATES THE ROOT MEAN SQUARE OF THE DEVIATIONS OF                          CRA03130
* PREDICTED CONCENTRATION VALUES FROM EXPERIMENTAL VALUES                       CRA03140
************************************************************                    CRA03150
*                                                                               CRA03160
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                     CRA03170
      PARAMETER ( N = 20 )                                                      CRA03180
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),SQTAU(N),                  CRA03190
     /          ETAU(N),CCAL(N),UPCAL(N),UPEXP(N)                              CRA03200
                                                                                CRA03210
      DO 10 I = 1, NEXP                                                         CRA03220
      ETAU(I) = (DP/X)*TEXP(I)*60.0**2/RS**2                                    CRA03230
  10  CONTINUE                                                                  CRA03240
                                                                                CRA03250
      RMS = 0.0                                                                 CRA03260
      RMS2 = 0.0                                                                CRA03270
                                                                                CRA03280
      DO 100 I = 2, NEXP                                                        CRA03290
      ISCAN = 0                                                                 CRA03300
```

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```
   20 CONTINUE                                                          CRA03310
      ISCAN = ISCAN + 1                                                 CRA03320
      IF ( ETAU(I) .GT. TAU(ISCAN) ) GOTO 20                            CRA03330
*                                                                       CRA03340
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                         CRA03350
*                                                                       CRA03360
      CCAL(I)=(CBAR(ISCAN)-CBAR(ISCAN+1))*((ETAU(IEXP)-TAU(ISCAN))/     CRA03370
     /        (TAU(ISCAN) - TAU(ISCAN+1))) + CBAR(ISCAN+1)             CRA03380
                                                                        CRA03390
      IF ( I .NE. 1 ) THEN                                              CRA03400
      RMS2 = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS2                    CRA03410
      ELSE                                                              CRA03420
      ENDIF                                                             CRA03430
      RMS = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS                      CRA03440
                                                                        CRA03450
      SQTAU(I) = SQRT( ETAU(I) )                                        CRA03460
      UPCAL(I) = ABS(1.0 - CCAL(I) )/( 1.0 - CEOCO )                    CRA03470
      UPEXP(I) = ABS(1.0 - CEXP(I) )/( 1.0 - CEOCO )                    CRA03480
                                                                        CRA03490
      PRINT*, CCAL(I), UPCAL(I)                                         CRA03500
                                                                        CRA03510
                                                                        CRA03520
  100 CONTINUE                                                          CRA03530
                                                                        CRA03540
      RMS = 100.0*SQRT(RMS/REAL(NEXP))                                  CRA03550
      RMS2 = 100.0*SQRT(RMS2/REAL(NEXP-1))                              CRA03560
      DSFIT = DP/X                                                      CRA03570
                                                                        CRA03580
      RETURN                                                            CRA03590
      END                                                               CRA03600
                                                                        CRA03610
*************************************************************************CRA03620
      BLOCK DATA                                                        CRA03630
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                              CRA03640
      DOUBLE PRECISION KF,NF                                            CRA03650
      PARAMETER ( N =20 )                                               CRA03660
      DIMENSION TEXP(N), CEXP(N)                                        CRA03670
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           CRA03680
      COMMON /INDATA2/RHOP,CO,TEMP                                      CRA03690
      COMMON /INEXP/TEXP,CEXP                                           CRA03700
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                 CRA03710
      COMMON /RRX/ CONST, ORDER1, ORDER2, RCONC                         CRA03720
                                                                        CRA03730
      DATA CONST, ORDER1, ORDER2, RCONC /200.0,-0.6,1.0,240.0/          CRA03740
                                                                        CRA03750
      DATA EPSI1, EPSI2, ERROR / 1.0D-8,1.0D-9,1.0D-13/                 CRA03760
                                                                        CRA03770
      DATA EP,RHOP,QS,DP,KF,CEOCO,TEMP,RS,NF,CO/0.63,0.67E6,0.25,       CRA03780
     / 1.3957E-6,0.1873,0.021,8.0,0.078,3.125,1000.0/                   CRA03790
                                                                        CRA03800
CCCCCCCCCCC    PH 7,TEMP 8 C; OXYGEN PURGED = 31.1 MG/L,C MASS = 28.6   CRA03810
      DATA TEXP /0.0,0.16,0.50,1.0,1.5,2.0,3.0,5.0,7.0,9.5,12.0,24.0,   CRA03820
     /           36.0,48.0,72.0,96.0,120.0,144.0,180.0,264.0/           CRA03830
      DATA CEXP / 1.0,0.747,0.587,0.467,0.376,0.351,0.322,0.291,        CRA03840
     /          0.279,0.267,0.244,0.197,0.179,0.151,0.110,0.084,       CRA03850
```

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```
     /          0.059,0.042,0.029,0.021/                                    CRA03860
                                                                            CRA03870
      END                                                                   CRA03880
*****************************************************************************CRA03890
                                                                            CRA03900
      SUBROUTINE INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,        CRA03910
     /                   Q,QMID, QAVG,CBAR )                              CRA03920
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                                  CRA03930
      DOUBLE PRECISION KF,NF,LAMBDA                                         CRA03940
      PARAMETER ( NN = 100 )                                                CRA03950
      DIMENSION Q(NN,0:1),QMID(NN), QAVG(0:1),CBAR(0:1)                     CRA03960
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                               CRA03970
      COMMON /INDATA2/RHOP,CO,TEMP                                          CRA03980
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                     CRA03990
                                                                            CRA04000
      PSI = EP/RHOP                                                         CRA04010
      CEQUIL = CO*CEOCO                                                     CRA04020
      UPTAKE  =  1.0D0 - CEOCO                                              CRA04030
      DTAU    = 2.1D0/DBLE( M )                                             CRA04040
      DR      = 1.0D0/DBLE( N-1 )                                           CRA04050
                                                                            CRA04060
      LAMBDA   = KF*CO**(1.0/NF)/( 1.0D0 + KF*CO**(1.0/NF) )                CRA04070
      QINFQO = KF*(CEQUIL)**(1.0D0/NF)/LAMBDA/                              CRA04080
     &          ( 1.0D0+KF*(CEQUIL)**(1.0D0/NF) )                           CRA04090
      ALPHA   =  (1.0D0 - CEOCO)/QINFQO                                     CRA04100
                                                                            CRA04110
*** INITIALIZATION : AT TAU = 0                                             CRA04120
      DO 10 I =  1,N                                                        CRA04130
      Q(I,0)   =  0.0D0                                                     CRA04140
      QMID(I)  =  EPSI2*DBLE(I)                                             CRA04150
  10  CONTINUE                                                              CRA04160
      QAVG(0)  =  0.0D0                                                     CRA04170
      CBAR(0)  =  1.0D0                                                     CRA04180
                                                                            CRA04190
      WRITE(7,*)   NF,KF,CO,CEOCO                                           CRA04200
      PRINT20, NF,KF,CO,CEOCO                                               CRA04210
   20 FORMAT(7X,' ADSORPTION OF PHENOL ON GAC ',                            CRA04220
     /     /,7X, 30('-'), /,                                                CRA04230
     /     /,3X,'LANGMUIR FREUNDLICH ISOTHERM CONSTANT      = ',F9.3,      CRA04240
     /     /,3X,'LANGMUIR FREUNDLICH EQUILIBRIUM PARAMETER  = ',F9.3,      CRA04250
     /     /,3X,'INITIAL CONCENTRATION       = ',F9.3,                      CRA04260
     /     /,3X,'CBAR AT INFINITY            = ',F9.3)                      CRA04270
                                                                            CRA04280
      PRINT30, LAMBDA, UPTAKE, QINFQO,ALPHA                                 CRA04290
   30 FORMAT( 1X, ' LAMBDA                    = ',F6.3,                    CRA04300
     / .     /,1X, ' UPTAKE                   = ',F6.3,                    CRA04310
     /       /,1X, ' QBAR AT INFINITY(QINFQO) = ',F6.3,                    CRA04320
     /       /,1X, ' ALPHA                    = ',F6.3 )                   CRA04330
                                                                            CRA04340
C     PRINT40, TEMP,OXY,CMASS                                               CRA04350
                                                                            CRA04360
      RETURN                                                                CRA04370
      END                                                                   CRA04380
                                                                            CRA04390
*****************************************************************************CRA04400
```

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```
      SUBROUTINE OUTPUT(N,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)  CRA04410
                                                                        CRA04420
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             CRA04430
      DIMENSION SQTAU(N),CTAU(N),DSCAL(N),UPCAL(N),UPEXP(N)             CRA04440
                                                                        CRA04450
      PRINT5                                                            CRA04460
 5    FORMAT(/,4X,'I',11X,'SQTAU(I)',9X,'UPEXP(I)',9X,'UPEXP(I)',/,     CRA04470
     /        65('=') )                                                CRA04480
      DO 10 I = 1, N                                                    CRA04490
 10   PRINT20,I, SQTAU(I), UPEXP(I), UPCAL(I)                          CRA04500
 20   FORMAT( 3X,I2, 5X,F12.6, 5X, F12.6,5X,F12.6,/ )                   CRA04510
                                                                        CRA04520
      PRINT30                                                           CRA04530
 30   FORMAT(/,4X,'I',11X,'CTAU(I)',9X,'DSCAL(I)',/,                    CRA04540
     /        45('=') )                                                CRA04550
      DO 40 I = 1, N                                                    CRA04560
 40   PRINT50,I, CTAU(I), DSCAL(I)                                      CRA04570
 50   FORMAT( 3X,I2, 5X,F12.6, 5X, E12.6,/ )                            CRA04580
      PRINT*, 'BEST FIT DS VALUE IS =', DSFIT                           CRA04590
      PRINT*, 'RMS VALUE IS  =', RMS2                                   CRA04600
                                                                        CRA04610
      RETURN                                                            CRA04620
      END                                                               CRA04630
                                                                        CRA04640
```

Appendix A4

Optimization Program to Calculate Parameters for Pore & Surface Diffusion with Reaction in Batch Systems.

FILE: A4 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
*************************************************************************   A4 00010
*                        APPENDIX A4                                    *   A4 00020
* OPTIMIZATION PROGRAM TO CALCULATE PARAMETERS FOR PORE & SURFACE       *   A4 00030
*             DIFFUSION WITH REACTION IN BATCH SYSTEMS                  *   A4 00040
*                                                                       *   A4 00050
*************************************************************************   A4 00060
C                                                                           A4 00070
C IMSL Name:  BCPOL/DBCPOL (Single/Double precision version)               A4 00080
C                                                                           A4 00090
C Purpose:    Minimize a function of N variables subject to bounds on       A4 00100
C             the variables using a direct search complex algorithm.        A4 00110
C                                                                           A4 00120
C Usage:      CALL BCPOL (FCN, N, XGUESS, IBTYPE, XLB, XUB, FTOL,           A4 00130
C                         MAXFCN, X, FVALUE)                                A4 00140
C                                                                           A4 00150
C   Variable declarations                                                   A4 00160
                                                                            A4 00170
      INTEGER    N                                                          A4 00180
      PARAMETER  (N=3)                                                      A4 00190
C                                                                           A4 00200
      INTEGER    IBTYPE, K, MAXFCN, NOUT                                    A4 00210
      REAL       FTOL, FVALUE, X(N), XGUESS(N), XLB(N), XUB(N)              A4 00220
      EXTERNAL   BCPOL, FCN, UMACH                                          A4 00230
C                                                                           A4 00240
      DATA  XGUESS/-0.7E0, 2.0E0, 24.E1/, XLB/-0.8E0, 1.0E0, 17.5E1/,       A4 00250
     &      XUB/-0.6E0, 3.0E0, 28.5E1 /                                     A4 00260
C                                                                           A4 00270
      FTOL   = 1.0E-5                                                       A4 00280
      IBTYPE = 0                                                            A4 00290
      MAXFCN = 300                                                          A4 00300
C                                                                           A4 00310
      CALL BCPOL (FCN, N, XGUESS, IBTYPE, XLB, XUB, FTOL, MAXFCN, X,        A4 00320
     &            FVALUE)                                                 A4 00330
C                                                                           A4 00340
      CALL UMACH (2, NOUT)                                                  A4 00350
      WRITE (NOUT,99) (X(K),K=1,N), FVALUE                                  A4 00360
   99 FORMAT ('  THE BEST ESTIMATE FOR THE MINIMUM VALUE OF THE', /,        A4 00370
     &       '  FUNCTION IS X = (', 3(2X,E12.6), ')', /, '  WITH ',        A4 00380
     &       'function value FVALUE = ', E12.6)                             A4 00390
C                                                                           A4 00400
      END                                                                   A4 00410
*************************************************************************   A4 00420
*   EXTERNAL FUNCTION TO BE MINIMIZED                                       A4 00430
                                                                            A4 00440
      SUBROUTINE FCN (N, X, F)                                              A4 00450
      INTEGER    N                                                          A4 00460
      REAL       X(N), F, ORDER1, ORDER2, RCONC                             A4 00470
*                                                                           A4 00480
                                                                            A4 00490
      ORDER1  = X(1)                                                        A4 00500
      ORDER2  = X(2)                                                        A4 00510
      RCONC   = X(3)                                                        A4 00520
                                                                            A4 00530
      CALL CRANK8N ( ORDER1, ORDER2, RCONC )                                A4 00540
                                                                            A4 00550
```

```
      F = RMS                                                          A4 00560
      RETURN                                                           A4 00570
      END                                                              A4 00580
                                                                       A4 00590
**********************************************************************  A4 00600
*                                                                      A4 00610
      SUBROUTINE  CRANK8N (ORDER1, ORDER2, RCONC )                     A4 00620
*                                                                      A4 00630
************************* APPENDIX A3  ************************        A4 00640
*                                                                      A4 00650
*                                                                      A4 00660
* LAGMUIR FREUNDLICH ISOTHERM : PORE AND SURFACE DIFFUSION MODEL       A4 00670
* WITH REACTION                                                        A4 00680
*                                                                      A4 00690
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                            A4 00700
      DOUBLE PRECISION KF,NF,LAMBDA                                    A4 00710
      PARAMETER(N=61,M=2000,NEXP=20 )                                  A4 00720
      DIMENSION Q(N,0:M),QNEW(N),QOLD(N),QAVG(0:M),QMID(N),            A4 00730
     / CBAR(0:M),TAU(0:M),A(N),B(N),C(N),D(N),                         A4 00740
     / CCAL(NEXP), TEXP(NEXP), CEXP(NEXP), ETAU(NEXP), DSCAL(NEXP),    A4 00750
     / CTAU(NEXP),SQTAU(NEXP),UPCAL(NEXP),UPEXP(NEXP), RTERM(NEXP)     A4 00760
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                          A4 00770
      COMMON /INDATA2/RHOP,CO,TEMP                                     A4 00780
      COMMON /INEXP/TEXP,CEXP                                          A4 00790
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                A4 00800
      COMMON /RRX/ CONST                                               A4 00810
C     COMMON /RRX/ CONST, ORDER1, ORDER2, RCONC                        A4 00820
                                                                       A4 00830
      EXTERNAL AVERAGE, THOMAS, LOAD, INTER, POLATE,RXN                A4 00840
                                                                       A4 00850
      CALL INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,         A4 00860
     /             Q,QMID, QAVG,CBAR )                                 A4 00870
                                                                       A4 00880
      DS = 0.98E-8                                                     A4 00890
      X  = DP/DS                                                       A4 00900
                                                                       A4 00910
*** GENERAL LOOP                                                       A4 00920
                                                                       A4 00930
      DO 400 J = 0, M-1                                                A4 00940
                                                                       A4 00950
      ISUME1 = 0                                                       A4 00960
      ISUME2 = 0                                                       A4 00970
      TAU(J) = REAL(J)*DTAU                                            A4 00980
  399 CONTINUE                                                         A4 00990
                                                                       A4 01000
      DO 20  I = 1, N                                                  A4 01010
   20 QOLD(I)  = Q(I,J)                                                A4 01020
                                                                       A4 01030
      IF ( ISUME1 .EQ. 0) THEN                                         A4 01040
                                                                       A4 01050
      QAVG(J+1) = QAVG(J) + EPSI1                                      A4 01060
      CHECK = EPSI1                                                    A4 01070
      ELSE                                                             A4 01080
                                                                       A4 01090
      CALL AVERAGE ( N,QNEW,DR,QAV )                                   A4 01100
```

```
      CHECK = ABS ( QAVG(J+1) - QAV )                                    A4 01110
      QAVG(J+1) = QAV                                                    A4 01120
                                                                         A4 01130
      ENDIF                                                              A4 01140
                                                                         A4 01150
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                               A4 01160
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/                A4 01170
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )                A4 01180
                                                                         A4 01190
      QNNEW     = Q(N,J+1)                                               A4 01200
                                                                         A4 01210
      IF ( ISUME2 .EQ. 0 ) THEN                                          A4 01220
                                                                         A4 01230
      DO 30 I = 1 , N                                                    A4 01240
 30   QMID(I) = QMID(I) + EPSI2*(I)                                      A4 01250
      ELSE                                                               A4 01260
      DO 40 I = 1 , N                                                    A4 01270
 40   QMID(I) = ( Q(I,J) + Q(I,J+1) )/ 2.0D0                             A4 01280
      ENDIF                                                              A4 01290
                                                                         A4 01300
      ISUME1 = ISUME1 + 1                                                A4 01310
      ISUME2 = ISUME2 + 1                                                A4 01320
                                                                         A4 01330
       DO 45 I = 1 , N                                                   A4 01340
 45    RTERM(I) = 0.0                                                    A4 01350
                                                                         A4 01360
** CALL SUBROUTINE LOAD TO SET UP THE TRIDIAGONAL MATRIX                 A4 01370
                                                                         A4 01380
      CALL LOAD (X,RTERM,N,DTAU,DR,QOLD,QMID,QNNEW,A,B,C,D,DS,LAMBDA)    A4 01390
                                                                         A4 01400
      CALL THOMAS ( N,A,B,C,D,QNEW )                                     A4 01410
                                                                         A4 01420
      DO 50 I = 1, N                                                     A4 01430
      Q(I,J+1) = QNEW(I)                                                 A4 01440
 50   CONTINUE                                                           A4 01450
      TAUJ = TAU(J)                                                      A4 01460
                                                                         A4 01470
      IF  ( (CHECK .GT. ERROR ) .AND. ( ISUME1 .LT. 50) ) GOTO 399       A4 01480
                                                                         A4 01490
      CALL RXN(N,TAUJ,DTAU,RS,DS,RCONC,ORDER1,ORDER2,CONST,QOLD,RTERM)   A4 01500
                                                                         A4 01510
      CALL LOAD (X,RTERM,N,DTAU,DR,QOLD,QMID,QNNEW,A,B,C,D,DS,LAMBDA)    A4 01520
                                                                         A4 01530
      CALL THOMAS ( N,A,B,C,D,QNEW )                                     A4 01540
                                                                         A4 01550
      CBAR(J+1) = CBAR(0)- ALPHA*QAVG(J+1)                               A4 01560
      Q(N,J+1)  = KF*( CO*CBAR(J+1) )**(1.0D0/NF)/LAMBDA/                A4 01570
     &            ( 1.0D0+KF*(CO*CBAR(J+1))**(1.0D0/NF) )                A4 01580
                                                                         A4 01590
      QNNEW     = Q(N,J+1)                                               A4 01600
                                                                         A4 01610
      DO 60 I = 1, N                                                     A4 01620
      Q(I,J+1) = QNEW(I)                                                 A4 01630
 60   CONTINUE                                                           A4 01640
                                                                         A4 01650
```

```
C     PRINT*, TAU(J) , CBAR(J)                                          A4 01660
      WRITE(7,*) TAU(J) , CBAR(J)                                       A4 01670
                                                                        A4 01680
  400 CONTINUE                                                          A4 01690
                                                                        A4 01700
                                                                        A4 01710
      CALL POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,             A4 01720
     /             CCAL.DSFIT.SQTAU,UPCAL,UPEXP,RMS,RMS2)               A4 01730
                                                                        A4 01740
      CALL INTER  ( M,NEXP,RS,X,CEOCO,CBAR.TAU.TEXP,                    A4 01750
     /              CEXP,CTAU,DSCAL)                                    A4 01760
                                                                        A4 01770
      CALL OUTPUT(NEXP,CTAU,DSCAL,DSFIT,SQTAU,UPCAL.UPEXP,RMS,RMS2)     A4 01780
                                                                        A4 01790
      END                                                               A4 01800
                                                                        A4 01810
*****************************************************************     A4 01820
                                                                        A4 01830
      SUBROUTINE THOMAS ( N,A,B.C,D,X)                                  A4 01840
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A4 01850
*************************************************                   A4 01860
* THOMAS ALGORYTHM FOR SOLVING A TRIDIAGONAL MATRIX        *          A4 01870
*************************************************                   A4 01880
                                                                        A4 01890
      PARAMETER( M =100)                                                A4 01900
      DIMENSION A(N),B(N),C(N),D(N),X(N),GAM(M),BET(M)                  A4 01910
                                                                        A4 01920
      BET(1) = B(1)                                                     A4 01930
      GAM(1) = D(1)/B(1)                                                A4 01940
      DO 320 I = 2, N                                                   A4 01950
      BET(I) = B(I) -  A(I)*C(I-1)/BET(I-1)                             A4 01960
      GAM(I) = ( D(I) - A(I)*GAM(I-1) )/BET(I)                          A4 01970
  320 CONTINUE                                                          A4 01980
      X(N) = GAM(N)                                                     A4 01990
      DO 330 I = N -1,1,-1                                              A4 02000
      IF (X(I+1) .LT. 1.0E-77 ) THEN                                    A4 02010
      X(I+1) = GAM(I)                                                   A4 02020
      ELSE                                                              A4 02030
      X(I) = GAM(I) - C(I)*X(I+1)/BET(I)                                A4 02040
      ENDIF                                                             A4 02050
 330  CONTINUE                                                          A4 02060
                                                                        A4 02070
      DO 333 I = 1,N                                                    A4 02080
 333  CONTINUE                                                          A4 02090
      RETURN                                                            A4 02100
      END                                                               A4 02110
                                                                        A4 02120
*****************************************************************     A4 02130
                                                                        A4 02140
      SUBROUTINE AVERAGE( N,Q,DR,QAVG)                                  A4 02150
* INTEGRATION VIA SIMPSON'S COMPOSITE RULE                             A4 02160
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               A4 02170
      DIMENSION Q(N)                                                    A4 02180
                                                                        A4 02190
      XI0 = Q(1)*0.0*0.0 +  Q(N)*1.0*1.0                                A4 02200
```

```
      XI1 = 0.0D0                                                       A4 02210
      XI2 = 0.0D0                                                       A4 02220
      DO 350  I = 2, N-1                                                A4 02230
      IF ( MOD(I,2) .EQ. 0 ) THEN                                       A4 02240
      XI2 = XI2 + Q(I)*( (DR*REAL(I-1))**2 )                            A4 02250
      ELSE                                                              A4 02260
      XI1 = XI1 + Q(I)*( (DR*REAL(I-1))**2 )                            A4 02270
      ENDIF                                                             A4 02280
  350 CONTINUE                                                          A4 02290
      XI = (DR/3.0D0)*( XI0  + 4.0D0*XI2 + 2.0D0*XI1 )                  A4 02300
      QAVG = 3.0D0*XI                                                   A4 02310
                                                                        A4 02320
      RETURN                                                            A4 02330
      END                                                               A4 02340
                                                                        A4 02350
*******************************************************************************A4 02360
      SUBROUTINE LOAD (X,RTERM,N,DTAU,DR,QOLD,QMID,QNNEW, A,B,C,D,DS,   A4 02370
     /                 LAMBDA )                                         A4 02380
                                                                        A4 02390
      IMPLICIT DOUBLE PRECISION ( A-H,O-Z)                              A4 02400
      DOUBLE PRECISION KF,NF,LAMBDA                                     A4 02410
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           A4 02420
      COMMON /INDATA2/RHOP,CO,TEMP                                      A4 02430
      PARAMETER ( M =100 )                                              A4 02440
      DIMENSION QOLD(N),QMID(N),A(M),B(M),C(M),D(M),P(M),F(M),          A4 02450
     /          PO(M),RTERM(N)                                         A4 02460
                                                                        A4 02470
      PHI = DTAU/DR**2                                                  A4 02480
      NM1 = N-1                                                         A4 02490
      PSI = EP/RHOP                                                     A4 02500
                                                                        A4 02510
      DO 10 I = 1, N                                                    A4 02520
                                                                        A4 02530
      IF ( QMID(I) .GT. 1.0 ) THEN                                      A4 02540
      QMID(I) = 0.999999990D0                                           A4 02550
      ELSE                                                              A4 02560
      ENDIF                                                             A4 02570
      CK = 1.0 - QL                                                     A4 02580
      IF  ( ( QL .LT. 0.0 ) .OR. (CK .LT. 0.0 ) ) THEN                  A4 02590
      DCDQ = 0.0                                                        A4 02600
      ELSE                                                              A4 02610
      QL = LAMBDA*QMID(I)                                               A4 02620
      DCDQ =(NF/(KF**NF)/QS)*(QL**(NF-1.0))/((1.0-QL)**(NF+1.0))        A4 02630
      ENDIF                                                             A4 02640
                                                                        A4 02650
* FOR PSD CONSTANT DS MODEL                                            A4 02660
*     PO(I)  = PSI*DCDQ*X + 1.0                                         A4 02670
* FOR PSD WITH VARIABLE DS MODEL                                       A4 02680
      PO(I)  = PSI*DCDQ*X + NF/(1.0D0 - LAMBDA*QMID(I) )                A4 02690
* FOR HSSD WITH VARIABLE DS MODEL                                      A4 02700
*     PO(I)  =  NF/(1.0D0 - LAMBDA*QMID(I) )                           A4 02710
                                                                        A4 02720
   10 CONTINUE                                                          A4 02730
                                                                        A4 02740
      DO 20 I = 2, NM1                                                  A4 02750
```

```
      F(I) =(PHI/4.0D0)*(2.0D0*PO(I)/DBLE(I-1)+(PO(I+1)-PO(I-1))/2.0D0 )A4 02760
   20 CONTINUE                                                          A4 02770
*                                                                       A4 02780
* BOUNDARY NODE 1                                                      A4 02790
*                                                                       A4 02800
      A(1) = 0.0                                                        A4 02810
      B(1) = 1.0D0 + 3.0D0*PHI*PO(1)                                    A4 02820
      C(1) = - 3.0D0*PHI*PO(1)                                          A4 02830
      D(1) =( 2.0D0 - B(1))*QOLD(1) - C(1)*QOLD(2)-RTERM(1)             A4 02840
*                                                                       A4 02850
* INTERIOR NODES 2 TO NM1                                              A4 02860
*                                                                       A4 02870
      DO 30 I = 2, NM1                                                  A4 02880
      A(I) = -PHI*PO(I)/2.0D0 + F(I)                                    A4 02890
      B(I) = 1.0D0 + PHI*PO(I)                                          A4 02900
      C(I) = -PHI*PO(I)/2.0D0 - F(I)                                    A4 02910
      D(I) =-A(I)*QOLD(I-1)+(2.0-B(I))*QOLD(I)-C(I)*QOLD(I+1)-RTERM(I)  A4 02920
  30  CONTINUE                                                          A4 02930
*                                                                       A4 02940
* BOUNDARY NODE N                                                      A4 02950
*                                                                       A4 02960
      A(N) = 0.0                                                        A4 02970
      B(N) = 1.0D0                                                      A4 02980
      C(N) = 0.0                                                        A4 02990
      D(N) = QNNEW - RTERM(N)                                           A4 03000
                                                                        A4 03010
      RETURN                                                            A4 03020
      END                                                               A4 03030
*************************************************************************A4 03040
      SUBROUTINE RXN (N,TAUJ, DTAU, RS,DS,RCONC,ORDER1,ORDER2,          A4 03050
     /                CONST,QOLD,RTERM)                                 A4 03060
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A4 03070
      DIMENSION QOLD(N),RTERM(N)                                        A4 03080
      TAUJO = 0.0                                                       A4 03090
                                                                        A4 03100
      SIGMA = RCONC*((RS**2/DS)**ORDER1)                                A4 03110
      T2 = TAUJ + DTAU/2.0                                              A4 03120
      TM =  (T2**ORDER1)*SIGMA                                          A4 03130
                                                                        A4 03140
      DO  20 I = 1, N                                                   A4 03150
      IF ( QOLD(I) .LT. 0.0 ) THEN                                      A4 03160
      RTERM(I) = DTAU*CONST*TM                                          A4 03170
      ELSE                                                              A4 03180
      RTERM(I) = DTAU*CONST*TM*(QOLD(I)**ORDER2)                        A4 03190
      ENDIF                                                             A4 03200
   20 CONTINUE                                                          A4 03210
                                                                        A4 03220
      RETURN                                                            A4 03230
      END                                                               A4 03240
                                                                        A4 03250
*************************************************************************A4 03260
                                                                        A4 03270
      SUBROUTINE INTER ( M,NEXP,RS,X,CEOCO,CBAR,TAU,TEXP,               A4 03280
     /                   CEXP,CTAU,DSCAL)                               A4 03290
*************************************************************          A4 03300
```

```
FILE: A4       FORTRAN  A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY.                  A4 03310
* THE DIFFUSIVITY COEFFICIENT IS CALCULATED FROM THE        *           A4 03320
* RELATION : DSCAL = TAU*RS*RS/TIME                         *           A4 03330
*                                                           *           A4 03340
*************************************************************           A4 03350
*                                                                       A4 03360
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A4 03370
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),CTAU(NEXP),        A4 03380
     /          DSCAL(NEXP)                                            A4 03390
                                                                        A4 03400
      DO 100 IEXP = 2, NEXP                                             A4 03410
*                                                                       A4 03420
* SCAN THROUGH THE DATA                                                 A4 03430
*                                                                       A4 03440
      ISCAN = 0                                                         A4 03450
   10 CONTINUE                                                          A4 03460
      ISCAN = ISCAN + 1                                                 A4 03470
      IF ( CEXP(IEXP) .LT. CBAR(ISCAN) ) GOTO 10                        A4 03480
*                                                                       A4 03490
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME :                       A4 03500
*                                                                       A4 03510
      CTAU(IEXP) = ( TAU(ISCAN) - TAU(ISCAN+1) )                        A4 03520
     /             *( ( CEXP(IEXP) - CBAR(ISCAN+1))/                  A4 03530
     /             (CBAR(ISCAN)-CBAR(ISCAN+1))) + TAU(ISCAN+1)        A4 03540
      DPCAL = CTAU(IEXP)*RS*RS/( TEXP(IEXP)*60.0**2)                    A4 03550
      DSCAL(IEXP) = DPCAL*X                                             A4 03560
                                                                        A4 03570
  100 CONTINUE                                                          A4 03580
                                                                        A4 03590
      RETURN                                                            A4 03600
      END                                                               A4 03610
                                                                        A4 03620
*************************************************************************A4 03630
                                                                        A4 03640
      SUBROUTINE POLATE (M,NEXP,RS,CEOCO,X,CBAR,TAU,TEXP,DP,CEXP,       A4 03650
     /                   CCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)         A4 03660
                                                                        A4 03670
*************************************************************           A4 03680
* THIS SUBROUTINE INTERPOLATES  A SET OF DATA LINEARLY AND              A4 03690
* CALCULATES THE ROOT MEAN SQUARE OF THE DEVIATIONS OF                  A4 03700
* PREDICTED CONCENTRATION VALUES FROM EXPERIMENTAL VALUES               A4 03710
*************************************************************           A4 03720
*                                                                       A4 03730
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                             A4 03740
      PARAMETER ( N = 20 )                                              A4 03750
      DIMENSION CBAR(M),TAU(M),TEXP(NEXP),CEXP(NEXP),SQTAU(N),          A4 03760
     /          ETAU(N),CCAL(N),UPCAL(N),UPEXP(N)                      A4 03770
                                                                        A4 03780
      DO 10 I = 1, NEXP                                                 A4 03790
      ETAU(I) = (DP/X)*TEXP(I)*60.0**2/RS**2                            A4 03800
   10 CONTINUE                                                          A4 03810
                                                                        A4 03820
      RMS = 0.0                                                         A4 03830
      RMS2 = 0.0                                                        A4 03840
                                                                        A4 03850
```

```
      DO 100 I = 2, NEXP                                                A4 03860
      ISCAN = 0                                                         A4 03870
   20 CONTINUE                                                          A4 03880
      ISCAN = ISCAN + 1                                                 A4 03890
      IF ( ETAU(I) .GT. TAU(ISCAN) ) GOTO 20                            A4 03900
*                                                                       A4 03910
* INTERPOLATE USING LINEAR INTERPOLATION SCHEME                         A4 03920
*                                                                       A4 03930
      CCAL(I)=(CBAR(ISCAN)-CBAR(ISCAN+1))*((ETAU(IEXP)-TAU(ISCAN))/     A4 03940
     /        (TAU(ISCAN) - TAU(ISCAN+1))) + CBAR(ISCAN+1)              A4 03950
                                                                        A4 03960
      IF ( I .NE. 1 ) THEN                                              A4 03970
      RMS2 = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS2                    A4 03980
      ELSE                                                              A4 03990
      ENDIF                                                             A4 04000
      RMS = ( (CEXP(I)-CCAL(I))/CEXP(I) )**2 + RMS                      A4 04010
                                                                        A4 04020
      SQTAU(I) = SQRT( ETAU(I) )                                        A4 04030
      UPCAL(I) = ABS(1.0 - CCAL(I) )/( 1.0 - CEOCO )                    A4 04040
      UPEXP(I) = ABS(1.0 - CEXP(I) )/( 1.0 - CEOCO )                    A4 04050
                                                                        A4 04060
      PRINT*, CCAL(I), UPCAL(I)                                         A4 04070
                                                                        A4 04080
                                                                        A4 04090
  100 CONTINUE                                                          A4 04100
                                                                        A4 04110
      RMS = 100.0*SQRT(RMS/REAL(NEXP))                                  A4 04120
      RMS2 = 100.0*SQRT(RMS2/REAL(NEXP-1))                              A4 04130
      DSFIT = DP/X                                                      A4 04140
                                                                        A4 04150
      RETURN                                                            A4 04160
      END                                                               A4 04170
                                                                        A4 04180
*************************************************************************A4 04190
      BLOCK DATA                                                        A4 04200
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                              A4 04210
      DOUBLE PRECISION KF,NF                                            A4 04220
      PARAMETER ( N =20 )                                               A4 04230
      DIMENSION TEXP(N), CEXP(N)                                        A4 04240
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                           A4 04250
      COMMON /INDATA2/RHOP,CO,TEMP                                      A4 04260
      COMMON /INEXP/TEXP,CEXP                                           A4 04270
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                 A4 04280
C     COMMON /RRX/ CONST, ORDER1, ORDER2, RCONC                         A4 04290
      COMMON /RRX/ CONST                                                A4 04300
                                                                        A4 04310
C     DATA CONST, ORDER1, ORDER2, RCONC /200.0,-0.6,1.0,240.0/          A4 04320
      DATA CONST /200.0/                                                A4 04330
                                                                        A4 04340
      DATA EPSI1, EPSI2, ERROR / 1.0D-8,1.0D-9,1.0D-13/                 A4 04350
                                                                        A4 04360
      DATA EP,RHOP,QS,DP,KF,CEOCO,TEMP,RS,NF,CO/0.63,0.67E6,0.25,       A4 04370
     / 1.3957E-6,0.1873,0.021,8.0,0.078,3.125,1000.0/                   A4 04380
                                                                        A4 04390
CCCCCCCCCCC    PH 7,TEMP 8 C: OXYGEN PURGED = 31.1 MG/L,C MASS = 28.6   A4 04400
```

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FILE: A4        FORTRAN  A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS. DHAHRAN

      DATA TEXP /0.0,0.16,0.50,1.0,1.5,2.0,3.0,5.0,7.0,9.5,12.0,24.0.   A4 04410
     /          36.0,48.0,72.0,96.0,120.0,144.0,180.0,264.0/           A4 04420
      DATA CEXP / 1.0,0.747,0.567,0.467,0.376,0.351,0.322,0.291.        A4 04430
     /          0.279,0.267,0.244,0.197,0.179,0.151,0.110,0.084.       A4 04440
     /          0.059,0.042,0.029,0.021/                               A4 04450
                                                                       A4 04460
      END                                                              A4 04470
*********************************************************************A4 04480
                                                                       A4 04490
      SUBROUTINE INITIA (N,M,PSI,CEQUIL,DTAU,DR,LAMBDA,QINFQO,ALPHA,   A4 04500
     /                   Q,QMID, QAVG,CBAR )                           A4 04510
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                             A4 04520
      DOUBLE PRECISION KF,NF,LAMBDA                                    A4 04530
      PARAMETER ( NN = 100 )                                           A4 04540
      DIMENSION Q(NN,0:1),QMID(NN), QAVG(0:1),CBAR(0:1)                A4 04550
      COMMON /INDATA1/EP,QS,DP,KF,CEOCO,RS,NF                          A4 04560
      COMMON /INDATA2/RHOP,CO,TEMP                                     A4 04570
      COMMON /EPSI/ EPSI1, EPSI2, ERROR                                A4 04580
                                                                       A4 04590
      PSI = EP/RHOP                                                    A4 04600
      CEQUIL = CO*CEOCO                                                A4 04610
      UPTAKE  =  1.0D0 - CEOCO                                         A4 04620
      DTAU    = 2.1D0/DBLE( M )                                        A4 04630
      DR      = 1.0D0/DBLE( N-1 )                                      A4 04640
                                                                       A4 04650
      LAMBDA   = KF*CO**(1.0/NF)/( 1.0D0 + KF*CO**(1.0/NF) )           A4 04660
      QINFQO = KF*(CEQUIL)**(1.0D0/NF)/LAMBDA/                         A4 04670
     &          ( 1.0D0+KF*(CEQUIL)**(1.0D0/NF) )                      A4 04680
      ALPHA   =  (1.0D0 - CEOCO)/QINFQO                                A4 04690
                                                                       A4 04700
*** INITIALIZATION : AT TAU = 0                                        A4 04710
      DO 10 I =  1,N                                                   A4 04720
      Q(I,0)   =  0.0D0                                                A4 04730
      QMID(I)  =  EPSI2*DBLE(I)                                        A4 04740
  10  CONTINUE                                                         A4 04750
      QAVG(0)  =  0.0D0                                                A4 04760
      CBAR(0)  =  1.0D0                                                A4 04770
                                                                       A4 04780
      WRITE(7,*)   NF,KF,CO,CEOCO                                      A4 04790
      PRINT20, NF,KF,CO,CEOCO                                          A4 04800
   20 FORMAT(7X,' ADSORPTION OF PHENOL ON GAC ',                       A4 04810
     /     /,7X, 30('-'), /,                                          A4 04820
     /     /,3X,'LANGMUIR FREUNDLICH ISOTHERM CONSTANT      = ',F9.3.  A4 04830
     /     /,3X,'LANGMUIR FREUNDLICH EQUILIBRIUM PARAMETER  = ',F9.3.  A4 04840
     /     /,3X,'INITIAL CONCENTRATION       = ',F9.3,                  A4 04850
     /     /,3X,'CBAR AT INFINITY            = ',F9.3)                  A4 04860
                                                                       A4 04870
      PRINT30, LAMBDA, UPTAKE, QINFQO,ALPHA                            A4 04880
   30 FORMAT( 1X, ' LAMBDA                   = ',F6.3,                 A4 04890
     /      /,1X, ' UPTAKE                   = ',F6.3,                 A4 04900
     /      /,1X, ' QBAR AT INFINITY(QINFQO) = ',F6.3,                 A4 04910
     /      /,1X, ' ALPHA                    = ',F6.3 )                A4 04920
                                                                       A4 04930
C     PRINT40, TEMP,OXY,CMASS                                          A4 04940
                                                                       A4 04950
```

FILE: A4 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
      RETURN                                                                A4 04960
      END                                                                   A4 04970
                                                                            A4 04980
*****************************************************************************A4 04990
      SUBROUTINE OUTPUT(N,CTAU,DSCAL,DSFIT,SQTAU,UPCAL,UPEXP,RMS,RMS2)      A4 05000
                                                                            A4 05010
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                 A4 05020
      DIMENSION SQTAU(N),CTAU(N),DSCAL(N),UPCAL(N),UPEXP(N)                 A4 05030
                                                                            A4 05040
      PRINT5                                                                A4 05050
 5    FORMAT(/,4X,'I',11X,'SQTAU(I)',9X,'UPEXP(I)',9X,'UPEXP(I)',/,         A4 05060
     /        65('=') )                                                    A4 05070
      DO 10 I = 1, N                                                        A4 05080
 10   PRINT20,I, SQTAU(I), UPEXP(I), UPCAL(I)                               A4 05090
 20   FORMAT( 3X,I2, 5X,F12.6, 5X, F12.6,5X,F12.6,/ )                       A4 05100
                                                                            A4 05110
      PRINT30                                                               A4 05120
 30   FORMAT(/,4X,'I',11X,'CTAU(I)',9X,'DSCAL(I)',/,                        A4 05130
     /        45('=') )                                                    A4 05140
      DO 40 I = 1, N                                                        A4 05150
 40   PRINT50,I, CTAU(I), DSCAL(I)                                          A4 05160
 50   FORMAT( 3X,I2, 5X,F12.6, 5X, E12.6,/ )                                A4 05170
      PRINT*, 'BEST FIT DS VALUE IS =', DSFIT                               A4 05180
      PRINT*, 'RMS VALUE IS  =', RMS2                                       A4 05190
                                                                            A4 05200
      RETURN                                                                A4 05210
      END                                                                   A4 05220
                                                                            A4 05230
```

Appendix A5

Program to Calculate Breakthrough Curves for Pore and Surface Diffusion Controlled Systems.

FILE: A5 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
********************  A5  ********************************          A5 00010
C                                                                   A5 00020
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                          A5 00030
      PARAMETER  (MXPARM=50,NT=112,MC=14,NC=7,MSTEP=300)            A5 00040
      PARAMETER  (MABSE=1, MBDF=2, MSOLVE=2)                        A5 00050
      DIMENSION Y(NT),CP(NT),YPRIME(NT),PARAM(MXPARM),TP(NT),CBAR(NT) A5 00060
      DIMENSION Q(NT)                                               A5 00070
      DOUBLE PRECISION KLF, NLF,L,KF,LAMBDA                         A5 00080
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO               A5 00090
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL                           A5 00100
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI             A5 00110
      COMMON/BLOCKB/ WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7) A5 00120
      EXTERNAL   DIVPAG, SSET, UMACH, FCN, FCNJ,INPUT,ORTHOG        A5 00130
      CALL UMACH (2, NOUT)                                          A5 00140
                                                                    A5 00150
      CALL INPUT (TMAX)                                             A5 00160
                                                                    A5 00170
      CALL ORTHOG (WZ,AZ,BZ,WR,AR,BR)                               A5 00180
                                                                    A5 00190
      TPMAX = TMAX*V/( L*(1.0+DG) )                                 A5 00200
      DTP = TMAX/MSTEP                                              A5 00210
                                                                    A5 00220
      N = MC*NC + MC                                                A5 00230
      MNC = MC*NC                                                   A5 00240
      T = 0.0                                                       A5 00250
      TP(1) = 0.0                                                   A5 00260
      CBAR(1) = 0.0                                                 A5 00270
      DO 10 I   = 1, N                                              A5 00280
      CP(I) = 0.0                                                   A5 00290
      Y(I) = 0.0                                                    A5 00300
 10   CONTINUE                                                      A5 00310
      TOL = 1.E-3                                                   A5 00320
      CALL SSET (MXPARM, 0.0, PARAM, 1)                             A5 00330
      PARAM(10) = MABSE                                             A5 00340
      PARAM(12) = MBDF                                              A5 00350
      PARAM(13) = MSOLVE                                            A5 00360
                                                                    A5 00370
      IDO = 1                                                       A5 00380
                                                                    A5 00390
      DO 100 I = 2, MSTEP                                           A5 00400
      TP(I) = TP(I-1) + DPT                                         A5 00410
      TEND = TP(I)                                                  A5 00420
                                                                    A5 00430
      CALL DIVPAG (IDO, N, FCN, FCNJ, A, T, TEND, TOL, PARAM, Y)    A5 00440
                                                                    A5 00450
      CBAR(I) = Y(N)                                                A5 00460
                                                                    A5 00470
      IF (I .EQ. MSTEP) IDO = 3                                     A5 00480
                                                                    A5 00490
 100  CONTINUE                                                      A5 00500
                                                                    A5 00510
      CALL POLATE(MSTEP, CBAR, TP)                                  A5 00520
                                                                    A5 00530
      END                                                           A5 00540
                                                                    A5 00550
```

```
FILE: A5       FORTRAN  A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS. DHAHRAN

*****************************************************************************   A5 00560
                                                                                A5 00570
      SUBROUTINE FCN ( N, T, Y, YPRIME )                                        A5 00580
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                     A5 00590
      DOUBLE PRECISION  L,KF,KLF, NLF, LAMBDA                                   A5 00600
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                           A5 00610
      COMMON /INPUT2/ KLF, NLF, CO, QE, DL                                      A5 00620
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI                         A5 00630
      COMMON/BLOCKB/ WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7)           A5 00640
      PARAMETER ( NC = 7, MC = 14, NN = 112  )                                  A5 00650
      DIMENSION Y(N),CP(NN), YPRIME(N),EDS(NN),Q(NN)                            A5 00660
      EXTERNAL ORTHOG                                                           A5 00670
                                                                                A5 00680
      ND = NC - 1                                                               A5 00690
      MD = MC - 1                                                               A5 00700
      MND = MC*ND                                                               A5 00710
      MNC = MC + MC*ND                                                          A5 00720
      N = MNC + MC                                                              A5 00730
*                                                                               A5 00740
      CIBAR = 1.0                                                               A5 00750
                                                                                A5 00760
      DGPS = 1.0 + DGP/DGS                                                      A5 00770
      DG = DGP + DGS                                                            A5 00780
      A = DGP/DG                                                                A5 00790
      B = DGS/DG/LAMBDA                                                         A5 00800
                                                                                A5 00810
      DO 9 I = 1, MNC                                                           A5 00820
      Q(I) = Y(I)                                                               A5 00830
      THETA = LAMBDA*Q(I)                                                       A5 00840
      IF( ( THETA .GT. 0.) .AND. (THETA .LT. 1.) )  THEN                        A5 00850
      CP(I) = ( THETA/(1.0 - THETA)/KLF)**NLF                                   A5 00860
      EDS(I) = EDSO*NLF/(1. - THETA )                                           A5 00870
      ELSE                                                                      A5 00880
      CP(I) = 0.0                                                               A5 00890
      EDS(I) = EDSO                                                             A5 00900
      ENDIF                                                                     A5 00910
  9   CONTINUE                                                                  A5 00920
*                                                                               A5 00930
* EVALUATING DX/DT(J,K,T)                                                       A5 00940
*                                                                               A5 00950
      KK = 0                                                                    A5 00960
      SUMWW  = 0.0                                                              A5 00970
      SUMWX  = 0.0                                                              A5 00980
      SUMDX  = 0.0                                                              A5 00990
                                                                                A5 01000
      DO 40 K = 1, MC                                                           A5 01010
      SUMDX = 0.0                                                               A5 01020
      DO 30 J = 1, NC - 1                                                       A5 01030
      SUMAX = AR(NC,J)*Y(MND+K)                                                 A5 01040
      SUMAC = AR(NC,J)*CP(MND+K)                                                A5 01050
      SUMBC = (EDP - DGP*EDS(KK+J)/DGS)*BR(NC,J)*CP(MND+K) +                    A5 01060
     /        (EDS(KK+J) + DGP*EDS(KK+J)/DGS)*BR(NC,J)*Y(MND+K)                 A5 01070
      DO 20 I = 1, NC-1                                                         A5 01080
                                                                                A5 01090
      SUMAX = SUMAX + AR(I,J)*Y(KK+I)                                           A5 01100
```

```
      SUMAC = SUMAC + AR(I,J)*CP(KK+I)                                  A5 01110
      SUMBC = SUMBC + (EDP - DGP*EDS(KK+J)/DGS)*BR(I,J)*CP(KK+I) +      A5 01120
     /        (EDS(KK+J) + DGP*EDS(KK+J)/DGS)*BR(I,J)*Y(KK+I)          A5 01130
   20 CONTINUE                                                          A5 01140
      AXAC = (- DGP/DGS)*EDSO*NLF*LAMBDA/((1.-LAMBDA*Y(KK+J))**2)       A5 01150
     /       *SUMAX*SUMAC                                               A5 01160
      AXSQ =( (1.+DGP/DGS)*EDSO*NLF*LAMBDA/((1.-LAMBDA*Y(KK+J))**2))*   A5 01170
     /         SUMAX**2                                                 A5 01180
      YPRIME(KK+J) =  ( (DG + 1.0)/DG )*( SUMBC - AXAC + AXSQ )         A5 01190
      SUMDX = SUMDX + ( WR(J)/WR(NC) )*YPRIME(KK+J)                     A5 01200
      SUMWX = SUMWX + WR(J)*YPRIME(KK+J)                                A5 01210
   30 CONTINUE                                                          A5 01220
      SUMDX = SUMDX + ( WR(NC)/WR(NC) )*YPRIME(MND+K)                   A5 01230
      SUMWX = SUMWX + WR(NC)*YPRIME(MND+K)                              A5 01240
                                                                        A5 01250
      YPRIME(MND+K) = ((DG+1.0)/(DG*WR(NC)))*ST*(Y(MNC+K)-CP(MND+K))    A5 01260
     /              -SUMDX                                             A5 01270
      SUMWW = SUMWW + WZ(K)*SUMWX                                       A5 01280
      KK = KK + NC - 1                                                  A5 01290
   40 CONTINUE                                                          A5 01300
                                                                        A5 01310
* EVALUATING DC8/DT(K,T)                                               A5 01320
                                                                        A5 01330
      AAC = 0.0                                                         A5 01340
      WAC = 0.0                                                         A5 01350
      DO 60 K = 2, MC-1                                                 A5 01360
      PC = 0.0                                                          A5 01370
      DO 50 I = 1, MC                                                   A5 01380
      PC = PC + (1.+DG)*( BZ(I,K)/PE - AZ(I,K) )*Y(MNC+I)               A5 01390
   50 CONTINUE                                                          A5 01400
      PC = PC - 3.0*(DG+1.0)*ST*( Y(MNC+K) - CP(MND+K) )                A5 01410
      YPRIME(MNC+K) = PC                                                A5 01420
      AAC = AAC + PC*AZ(MC,K)/AZ(MC,MC)                                 A5 01430
      WAC = WAC + ( WZ(K)-WZ(MC)*AZ(MC,K)/AZ(MC,MC))*PC                 A5 01440
   60 CONTINUE                                                          A5 01450
                                                                        A5 01460
* AT THE ENTRNACE :                                                    A5 01470
      WWA = WZ(1) - WZ(MC)*AZ(MC,1)/AZ(MC,MC)                           A5 01480
      YPRIME(MNC+1) =( ((DG+1.0)*(CIBAR-Y(N))-WAC)-3*DG*SUMWW )/WWA     A5 01490
* AT EXIT                                                              A5 01500
      YPRIME(N) = -AAC - (AZ(MC,1)/AZ(MC,MC))*YPRIME(MNC+1)             A5 01510
                                                                        A5 01520
      RETURN                                                            A5 01530
      END                                                               A5 01540
                                                                        A5 01550
*************************************************************************A5 01560
                                                                        A5 01570
      SUBROUTINE FCNJ (N, T, Y, DYPDY)                                  A5 01580
C     SPECIFICATIONS FOR ARGUMENTS                                      A5 01590
      INTEGER    N                                                      A5 01600
      REAL       T, Y(N), DYPDY(N,*)                                    A5 01610
C                                                                       A5 01620
      RETURN                                                            A5 01630
      END                                                               A5 01640
                                                                        A5 01650
```

```
*****************************************************************      A5 01660
      SUBROUTINE INPUT (TMAX)                                          A5 01670
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                             A5 01680
      PARAMETER (NEXP = 49)                                            A5 01690
      DOUBLE PRECISION L, KLF, NLF, KF, LAMBDA                         A5 01700
      DIMENSION TAU(NEXP), CEXP(NEXP)                                  A5 01710
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                  A5 01720
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL                              A5 01730
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI                A5 01740
      COMMON/EXP/TAU,CEXP                                              A5 01750
                                                                       A5 01760
      READ*, KLF,NLF,CO,QE,DL                                          A5 01770
      READ*, V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                           A5 01780
      READ*, ( TAU(I), I = 1, NEXP)                                    A5 01790
      READ*, ( CEXP(I), I = 1, NEXP)                                   A5 01800
      TMAX = TAU(NEXP)                                                 A5 01810
                                                                       A5 01820
      PE = V*L/DL                                                      A5 01830
      ST = KF*L*(1.-EPSI)/(R*EPSI*V)                                   A5 01840
      DGP = (1.-EPSI)*EPSIP/EPSI                                       A5 01850
      DGS = (1.-EPSI)*RHOP*QE/(EPSI*CO)                                A5 01860
      DG = DGS + DGP                                                   A5 01870
      EDP = L*DP*DGP/(R**2*V)                                          A5 01880
      EDSO = L*DSO*DGS/(R**2*V)                                        A5 01890
      PHI = KLF*CO*(1./NLF)                                            A5 01900
      LAMBDA = PHI/(1.+PHI)                                            A5 01910
                                                                       A5 01920
C     PRINT1, V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                          A5 01930
C  1  FORMAT( 4(E12.6,2X ) )                                           A5 01940
                                                                       A5 01950
      PRINT2, DGS,EDSO                                                 A5 01960
      PRINT2, PE,ST,DGP,DGP/DGS,DGS,EDP,EDSO,LAMBDA,PHI                A5 01970
   2  FORMAT( 4(E12.6,2X ) )                                           A5 01980
      END                                                              A5 01990
                                                                       A5 02000
*****************************************************************      A5 02010
                                                                       A5 02020
       SUBROUTINE ORTHOG (WZ,AZ,BZ,WR,AR,BR)                           A5 02030
       IMPLICIT DOUBLE PRECISION(A-H, O-Z)                             A5 02040
       DIMENSION WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7)      A5 02050
                                                                       A5 02060
*THE NUMBER OF RADIAL COLLOC PTS, THE WR VECTOR, AND THE AR.BR         A5 02070
* MATRICES ARE READ IN :                                              A5 02080
*                                                                      A5 02090
       READ*, NC                                                       A5 02100
       PRINT*, NC                                                      A5 02110
       READ*, ( WR(I), I=1, NC )                                       A5 02120
       PRINT*, ( WR(I), I=1, NC )                                      A5 02130
                                                                       A5 02140
       DO 5 I =1, NC                                                   A5 02150
       READ*, ( AR(I,J), J=1, NC )                                     A5 02160
       PRINT*,( AR(I,J), J=1, NC )                                     A5 02170
 5     CONTINUE                                                        A5 02180
                                                                       A5 02190
       DO 10 I =1, NC                                                  A5 02200
```

```
      READ*, ( BR(I,J), J=1, NC )                                        A5 02210
      PRINT*,( BR(I,J), J=1, NC )                                        A5 02220
 10   CONTINUE                                                           A5 02230
                                                                         A5 02240
*THE NUMBER OF AXIAL COLLOC PTS, THE WZ VECTOR, AND THE AZ AND BZ        A5 02250
*MATRICES ARE READ IN :                                                  A5 02260
*                                                                        A5 02270
      READ*, MC                                                          A5 02280
      PRINT*, MC                                                         A5 02290
      READ*,( WZ(I), I=1, MC )                                           A5 02300
      PRINT100,( WZ(I), I=1, MC )                                        A5 02310
                                                                         A5 02320
      DO 20 I =1, MC                                                     A5 02330
      READ*, ( AZ(I,J), J=1, MC )                                        A5 02340
      PRINT100,( AZ(I,J), J=1, MC )                                      A5 02350
 20   CONTINUE                                                           A5 02360
                                                                         A5 02370
      DO 30 I =1, MC                                                     A5 02380
      READ*, ( BZ(I,J), J=1, MC )                                        A5 02390
      PRINT100,( BZ(I,J), J=1, MC )                                      A5 02400
 30   CONTINUE                                                           A5 02410
                                                                         A5 02420
      RETURN                                                             A5 02430
 100  FORMAT( 4F20.12 )                                                  A5 02440
                                                                         A5 02450
      END                                                                A5 02460
                                                                         A5 02470
*************************************************************************A5 02480
                                                                         A5 02490
      SUBROUTINE POLATE (N, CBAR, TP)                                    A5 02500
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                               A5 02510
      PARAMETER (NEXP = 49)                                              A5 02520
      DOUBLE PRECISION L, KLF, NLF, KF, LAMBDA                           A5 02530
      DIMENSION TAU(NEXP), CEXP(NEXP),TPE(NEXP),TAU(NEXP),CEXP(NEXP),    A5 02540
     /          CCAL(NEXP),CBAR(N),TP(N)                                A5 02550
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                    A5 02560
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL                                A5 02570
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI                  A5 02580
      COMMON/EXP/TAU,CEXP                                                A5 02590
                                                                         A5 02600
      DO 10 I = 1, NEXP                                                  A5 02610
 10   TPE(I) = TAU(I)*V/L/(1+DG)                                         A5 02620
                                                                         A5 02630
      RMS = 0.0                                                          A5 02640
      DO 100 I = 2, NEXP                                                 A5 02650
      ISCAN = 0                                                          A5 02660
 20   CONTINUE                                                           A5 02670
      ISCAN = ISCAN +1                                                   A5 02680
      IF( TPE(I) .GT. TP(ISCAN) ) GOTO 20                                A5 02690
                                                                         A5 02700
                                                                         A5 02710
      CCAL(I) = (CAR(ISCAN)-CBAR(ISCAN+1))*((TPE(I)-TPE(ISCAN))/         A5 02720
     /          (TPE(ISCAN)-TPE(ISCAN+1))) + CBAR(ISCAN+1)               A5 02730
                                                                         A5 02740
      RMS = RMS + ((CEXP(I)-CCAL(I))/CEXP(I))**2                         A5 02750
```

```
                                                                    A5 02760
 100  CONTINUE                                                      A5 02770
                                                                    A5 02780
* PRINT OUT                                                        A5 02790
      DO 30 I = 2, NEXP                                             A5 02800
 30   PRINT200, TPE(I), CCAL(I), CEXP(I)                           A5 02810
 200  FORMAT (2X, 4(E22.14, 2X) )                                   A5 02820
                                                                    A5 02830
      RETURN                                                        A5 02840
      END                                                           A5 02850
```

Appendix A6

Program to Calculate Breakthrough Curves for Pore and Surface Diffusion Controlled Systems involving Reaction.

FILE: A6 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

```
********************  A6  ************************************  A6 00010
C                                                               A6 00020
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                      A6 00030
      PARAMETER  (MXPARM=50,NT=112,MC=14,NC=7,MSTEP=300)        A6 00040
      PARAMETER  (MABSE=1, MBDF=2, MSOLVE=2)                    A6 00050
      DIMENSION Y(NT),CP(NT),YPRIME(NT),PARAM(MXPARM),TP(NT),CBAR(NT)  A6 00060
      DIMENSION Q(NT)                                           A6 00070
      DOUBLE PRECISION KLF, NLF,L,KF,LAMBDA                     A6 00080
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO           A6 00090
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL,RK                    A6 00100
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI         A6 00110
      COMMON/BLOCKB/ WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7)  A6 00120
      EXTERNAL   DIVPAG, SSET, UMACH, FCN, FCNJ,INPUT,ORTHOG    A6 00130
      CALL UMACH (2, NOUT)                                      A6 00140
                                                                A6 00150
      CALL INPUT (TMAX)                                         A6 00160
                                                                A6 00170
      CALL ORTHOG (WZ,AZ,BZ,WR,AR,BR)                           A6 00180
                                                                A6 00190
      TPMAX = TMAX*V/( L*(1.0+DG) )                             A6 00200
      DTP = TMAX/MSTEP                                          A6 00210
                                                                A6 00220
      N = MC*NC + MC                                            A6 00230
      MNC = MC*NC                                               A6 00240
      T = 0.0                                                   A6 00250
      TP(1) = 0.0                                               A6 00260
      CBAR(1) = 0.0                                             A6 00270
      DO 10 I   = 1, N                                          A6 00280
      CP(I) = 0.0                                               A6 00290
      Y(I) = 0.0                                                A6 00300
 10   CONTINUE                                                  A6 00310
      TOL = 1.E-3                                               A6 00320
      CALL SSET (MXPARM, 0.0, PARAM, 1)                         A6 00330
      PARAM(10) = MABSE                                         A6 00340
      PARAM(12) = MBDF                                          A6 00350
      PARAM(13) = MSOLVE                                        A6 00360
                                                                A6 00370
      IDO = 1                                                   A6 00380
                                                                A6 00390
      DO 100 I = 2, MSTEP                                       A6 00400
      TP(I) = TP(I-1) + DPT                                     A6 00410
      TEND = TP(I)                                              A6 00420
                                                                A6 00430
      CALL DIVPAG (IDO, N, FCN, FCNJ, A, T, TEND, TOL, PARAM, Y)  A6 00440
                                                                A6 00450
      CBAR(I) = Y(N)                                            A6 00460
                                                                A6 00470
      IF (I .EQ. MSTEP) IDO = 3                                 A6 00480
                                                                A6 00490
 100  CONTINUE                                                  A6 00500
                                                                A6 00510
      CALL POLATE(MSTEP, CBAR, TP)                              A6 00520
                                                                A6 00530
      END                                                       A6 00540
                                                                A6 00550
```

FILE: A6 FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS. DHAHRAN

```
*************************************************************************  A6 00560
                                                                           A6 00570
      SUBROUTINE FCN ( N, T, Y, YPRIME )                                   A6 00580
      IMPLICIT DOUBLE PRECISION ( A-H, O-Z)                                A6 00590
      DOUBLE PRECISION  L,KF,KLF, NLF, LAMBDA                              A6 00600
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                      A6 00610
      COMMON /INPUT2/ KLF, NLF, CO, QE, DL,RK                              A6 00620
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI                    A6 00630
      COMMON/BLOCKB/ WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7)      A6 00640
      PARAMETER ( NC = 7, MC = 14, NN = 112  )                             A6 00650
      DIMENSION Y(N),CP(NN), YPRIME(N),EDS(NN),Q(NN)                       A6 00660
      EXTERNAL ORTHOG                                                      A6 00670
                                                                           A6 00680
      ND = NC - 1                                                          A6 00690
      MD = MC - 1                                                          A6 00700
      MND = MC*ND                                                          A6 00710
      MNC = MC + MC*ND                                                     A6 00720
      N = MNC + MC                                                         A6 00730
*                                                                          A6 00740
      CIBAR = 1.0                                                          A6 00750
                                                                           A6 00760
      DGPS = 1.0 + DGP/DGS                                                 A6 00770
      DG = DGP + DGS                                                       A6 00780
      A = DGP/DG                                                           A6 00790
      B = DGS/DG/LAMBDA                                                    A6 00800
      G = EPSIP*V*CO*RK/DGP/L                                              A6 00810
      M = 1                                                                A6 00820
                                                                           A6 00830
      DO 9 I = 1, MNC                                                      A6 00840
      Q(I) = Y(I)                                                          A6 00850
      THETA = LAMBDA*Q(I)                                                  A6 00860
      IF( ( THETA .GT. 0.) .AND. (THETA .LT. 1.) )  THEN                   A6 00870
      CP(I) = ( THETA/(1.0 - THETA)/KLF)**NLF                              A6 00880
      EDS(I) = EDSO*NLF/(1. - THETA )                                      A6 00890
      ELSE                                                                 A6 00900
      CP(I) = 0.0                                                          A6 00910
      EDS(I) = EDSO                                                        A6 00920
      ENDIF                                                                A6 00930
  9   CONTINUE                                                             A6 00940
*                                                                          A6 00950
* EVALUATING DX/DT(J,K,T)                                                 A6 00960
*                                                                          A6 00970
      KK = 0                                                               A6 00980
      SUMWW  = 0.0                                                         A6 00990
      SUMWX  = 0.0                                                         A6 01000
      SUMDX  = 0.0                                                         A6 01010
                                                                           A6 01020
      DO 40 K = 1, MC                                                      A6 01030
      SUMDX = 0.0                                                          A6 01040
      DO 30 J = 1, NC - 1                                                  A6 01050
                                                                           A6 01060
      IF(Q(MND+K) .LT. 0) .OR. (T .EQ. 0) ) THEN                           A6 01070
      RR = 0.0                                                             A6 01080
      ELSEIF (Q(MND+K) .EQ. 0) THEN                                        A6 01090
      RR = RK*T**(-0.6)                                                    A6 01100
```

```
      ELSE                                                              A6 01110
      RR = RK*T**(-0.6)*Q(MND+K)**M                                     A6 01120
      ENDIF                                                             A6 01130
                                                                        A6 01140
      SUMAX = AR(NC,J)*Y(MND+K)                                         A6 01150
      SUMAC = AR(NC,J)*CP(MND+K)                                        A6 01160
      SUMBC = (EDP - DGP*EDS(KK+J)/DGS)*BR(NC,J)*CP(MND+K) +            A6 01170
     / (EDS(KK+J) + DGP*EDS(KK+J)/DGS)*BR(NC,J)*Y(MND+K) - G*RR         A6 01180
      DO 20 I = 1, NC-1                                                 A6 01190
                                                                        A6 01200
      IF(Q(KK+I) .LT. 0) .OR. (T .EQ. 0) ) THEN                         A6 01210
      RR = 0.0                                                          A6 01220
      ELSEIF (Q(KK+I) .EQ. 0) THEN                                      A6 01230
      RR = RK*T**(-0.6)                                                 A6 01240
      ELSE                                                              A6 01250
      RR = RK*T**(-0.6)*Q(KK+I)**M                                      A6 01260
      ENDIF                                                             A6 01270
                                                                        A6 01280
      SUMAX = SUMAX + AR(I,J)*Y(KK+I)                                   A6 01290
      SUMAC = SUMAC + AR(I,J)*CP(KK+I)                                  A6 01300
      SUMBC = SUMBC + (EDP - DGP*EDS(KK+J)/DGS)*BR(I,J)*CP(KK+I) +      A6 01310
     /        (EDS(KK+J) + DGP*EDS(KK+J)/DGS)*BR(I,J)*Y(KK+I)-G*RR      A6 01320
   20 CONTINUE                                                          A6 01330
      AXAC = (- DGP/DGS)*EDSO*NLF*LAMBDA/((1.-LAMBDA*Y(KK+J))**2)       A6 01340
     /       *SUMAX*SUMAC                                               A6 01350
      AXSQ =( (1.+DGP/DGS)*EDSO*NLF*LAMBDA/((1.-LAMBDA*Y(KK+J))**2))*   A6 01360
     /         SUMAX**2                                                 A6 01370
      YPRIME(KK+J) =  ( (DG + 1.0)/DG )*( SUMBC - AXAC + AXSQ )         A6 01380
      SUMDX = SUMDX + ( WR(J)/WR(NC) )*YPRIME(KK+J)                     A6 01390
      SUMWX = SUMWX + WR(J)*YPRIME(KK+J)                                A6 01400
   30 CONTINUE                                                          A6 01410
      SUMDX = SUMDX + ( WR(NC)/WR(NC) )*YPRIME(MND+K)                   A6 01420
      SUMWX = SUMWX + WR(NC)*YPRIME(MND+K)                              A6 01430
                                                                        A6 01440
      YPRIME(MND+K) = ((DG+1.0)/(DG*WR(NC)))*ST*(Y(MNC+K)-CP(MND+K))    A6 01450
     /              -SUMDX                                             A6 01460
      SUMWW = SUMWW + WZ(K)*SUMWX                                       A6 01470
      KK = KK + NC - 1                                                  A6 01480
   40 CONTINUE                                                          A6 01490
                                                                        A6 01500
* EVALUATING DCB/DT(K,T)                                               A6 01510
                                                                        A6 01520
      AAC = 0.0                                                         A6 01530
      WAC = 0.0                                                         A6 01540
      DO 60 K = 2, MC-1                                                 A6 01550
      PC = 0.0                                                          A6 01560
      DO 50 I = 1, MC                                                   A6 01570
      PC = PC + (1.+DG)*( BZ(I,K)/PE - AZ(I,K) )*Y(MNC+I)               A6 01580
   50 CONTINUE                                                          A6 01590
      PC = PC - 3.0*(DG+1.0)*ST*( Y(MNC+K) - CP(MND+K) )                A6 01600
      YPRIME(MNC+K) = PC                                                A6 01610
      AAC = AAC + PC*AZ(MC,K)/AZ(MC,MC)                                 A6 01620
      WAC = WAC + ( WZ(K)-WZ(MC)*AZ(MC,K)/AZ(MC,MC))*PC                 A6 01630
   60 CONTINUE                                                          A6 01640
                                                                        A6 01650
```

```
* AT THE ENTRNACE :                                                    A6 01660
      WWA = WZ(1) - WZ(MC)*AZ(MC,1)/AZ(MC,MC)                          A6 01670
      YPRIME(MNC+1) =( ((DG+1.0)*(CIBAR-Y(N))-WAC)-3*DG*SUMWW )/WWA    A6 01680
* AT EXIT                                                             A6 01690
      YPRIME(N) = -AAC - (AZ(MC,1)/AZ(MC,MC))*YPRIME(MNC+1)            A6 01700
                                                                       A6 01710
      RETURN                                                           A6 01720
      END                                                              A6 01730
                                                                       A6 01740
*********************************************************************  A6 01750
                                                                       A6 01760
      SUBROUTINE FCNJ (N, T, Y, DYPDY)                                 A6 01770
C     SPECIFICATIONS FOR ARGUMENTS                                     A6 01780
      INTEGER    N                                                     A6 01790
      REAL       T, Y(N), DYPDY(N,*)                                   A6 01800
C                                                                      A6 01810
      RETURN                                                           A6 01820
      END                                                              A6 01830
                                                                       A6 01840
*********************************************************************  A6 01850
      SUBROUTINE INPUT (TMAX)                                          A6 01860
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                             A6 01870
      PARAMETER (NEXP = 49)                                            A6 01880
      DOUBLE PRECISION L, KLF, NLF, KF, LAMBDA                         A6 01890
      DIMENSION TAU(NEXP), CEXP(NEXP)                                  A6 01900
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                  A6 01910
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL,RK                           A6 01920
      COMMON /BLOCKA/ PE,ST,DGF,DGS,EDP,EDSO,LAMBDA,PHI                A6 01930
      COMMON/EXP/TAU,CEXP                                              A6 01940
                                                                       A6 01950
      READ*, KLF,NLF,CO,QE,DL,RK                                       A6 01960
      READ*, V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                           A6 01970
      READ*, ( TAU(I), I = 1, NEXP)                                    A6 01980
      READ*, ( CEXP(I), I = 1, NEXP)                                   A6 01990
      TMAX = T  NEXP)                                                  A6 02000
                                                                       A6 02010
      PE = V*L/DL                                                      A6 02020
      ST = KF*L*(1.-EPSI)/(R*EPSI*V)                                   A6 02030
      DGP = (1.-EPSI)*EPSIP/EPSI                                       A6 02040
      DGS = (1.-EPSI)*RHOP*QE/(EPSI*CO)                                A6 02050
      DG = DGS + DGP                                                   A6 02060
      EDP = L*DP*DGP/(R**2*V)                                          A6 02070
      EDSO = L*DSO*DGS/(R**2*V)                                        A6 02080
      PHI = KLF*CO*(1./NLF)                                            A6 02090
      LAMBDA = PHI/(1.+PHI)                                            A6 02100
                                                                       A6 02110
      END                                                              A6 02120
                                                                       A6 02130
*********************************************************************  A6 02140
                                                                       A6 02150
       SUBROUTINE ORTHOG (WZ,AZ,BZ,WR,AR,BR)                           A6 02160
       IMPLICIT DOUBLE PRECISION(A-H, O-Z)                             A6 02170
       DIMENSION WZ(14),AZ(14,14),BZ(14,14),WR(7),BR(7,7),AR(7,7)      A6 02180
                                                                       A6 02190
*THE NUMBER OF RADIAL COLLOC PTS. THE WR VECTOR. AND THE AR,BR         A6 02200
```

```
*  MATRICES ARE READ IN :                                                A6 02210
*                                                                        A6 02220
       READ*, NC                                                        A6 02230
       PRINT*, NC                                                       A6 02240
       READ*, ( WR(I), I=1, NC )                                        A6 02250
       PRINT*, ( WR(I), I=1, NC )                                       A6 02260
                                                                        A6 02270
       DO 5 I =1, NC                                                    A6 02280
       READ*, ( AR(I,J), J=1, NC )                                      A6 02290
       PRINT*,( AR(I,J), J=1, NC )                                      A6 02300
 5     CONTINUE                                                         A6 02310
                                                                        A6 02320
       DO 10 I =1, NC                                                   A6 02330
       READ*, ( BR(I,J), J=1, NC )                                      A6 02340
       PRINT*,( BR(I,J), J=1, NC )                                      A6 02350
 10    CONTINUE                                                         A6 02360
                                                                        A6 02370
*THE NUMBER OF AXIAL COLLOC PTS, THE WZ VECTOR, AND THE AZ AND BZ       A6 02380
*MATRICES ARE READ IN :                                                 A6 02390
*                                                                       A6 02400
       READ*, MC                                                        A6 02410
       PRINT*, MC                                                       A6 02420
       READ*,( WZ(I), I=1, MC )                                         A6 02430
       PRINT100,( WZ(I), I=1, MC )                                      A6 02440
                                                                        A6 02450
       DO 20 I =1, MC                                                   A6 02460
       READ*, ( AZ(I,J), J=1, MC )                                      A6 02470
       PRINT100,( AZ(I,J), J=1, MC )                                    A6 02480
 20    CONTINUE                                                         A6 02490
                                                                        A6 02500
       DO 30 I =1, MC                                                   A6 02510
       READ*, ( BZ(I,J), J=1, MC )                                      A6 02520
       PRINT100,( BZ(I,J), J=1, MC )                                    A6 02530
 30    CONTINUE                                                         A6 02540
                                                                        A6 02550
       RETURN                                                           A6 02560
 100   FORMAT( 4F20.12 )                                                A6 02570
                                                                        A6 02580
       END                                                              A6 02590
                                                                        A6 02600
*****************************************************************      A6 02610
                                                                        A6 02620
      SUBROUTINE POLATE (N, CBAR, TP)                                   A6 02630
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)                              A6 02640
      PARAMETER (NEXP = 49)                                             A6 02650
      DOUBLE PRECISION L, KLF, NLF, KF, LAMBDA                          A6 02660
      DIMENSION TAU(NEXP), CEXP(NEXP),TPE(NEXP),TAU(NEXP),CEXP(NEXP),   A6 02670
     /          CCAL(NEXP),CBAR(N),TP(N)                               A6 02680
      COMMON /INPUT1/ V,L,KF,EPSI,EPSIP,R,RHOP,DP,DSO                   A6 02690
      COMMON /INPUT2/ KLF, NLF, CO, QE,DL,RK                            A6 02700
      COMMON /BLOCKA/ PE,ST,DGP,DGS,EDP,EDSO,LAMBDA,PHI                 A6 02710
      COMMON/EXP/TAU,CEXP                                               A6 02720
                                                                        A6 02730
      DO 10 I = 1, NEXP                                                 A6 02740
 10   TPE(I) = TAU(I)*V/L/(1+DG)                                        A6 02750
```

```
                                                                      A6 02760
      RMS = 0.0                                                       A6 02770
      DO 100 I = 2, NEXP                                              A6 02780
      ISCAN = 0                                                       A6 02790
  20  CONTINUE                                                        A6 02800
      ISCAN = ISCAN +1                                                A6 02810
      IF( TPE(I) .GT. TP(ISCAN) ) GOTO 20                             A6 02820
                                                                      A6 02830
      CCAL(I) = (CAR(ISCAN)-CBAR(ISCAN+1))*((TPE(I)-TPE(ISCAN))/      A6 02840
     /          (TPE(ISCAN)-TPE(ISCAN+1))) + CBAR(ISCAN+1)           A6 02850
                                                                      A6 02860
      RMS = RMS + ((CEXP(I)-CCAL(I))/CEXP(I))**2                      A6 02870
                                                                      A6 02880
 100  CONTINUE                                                        A6 02890
                                                                      A6 02900
* PRINT OUT                                                          A6 02910
       DO 30 I = 2, NEXP                                              A6 02920
 30    PRINT200, TPE(I), CCAL(I), CEXP(I)                             A6 02930
 200   FORMAT (2X, 4(E22.14, 2X) )                                    A6 02940
                                                                      A6 02950
      RETURN                                                          A6 02960
      END                                                             A6 02970
```

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